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MANUFACTURE OF SOAP

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Manufacture of Soap

By

LINCOLN BURROWS

MANUFACTURING CHEMIST

MANUFACTURE OF SOAP
Parts 1–3

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MANUFACTURE OF SOAP

Serial 2055A (PART 1) Edition 1

INTRODUCTION

1. Definition of Soap.—Soap, strictly speaking, is the compound of an alkali, either sodium or potassium, with the higher fatty acids, especially with oleic, palmitic, and stearic acids. The insoluble compound of a fatty acid with a heavy metal is, however, technically called a soap. The chemist is familiar with the lead soap or lead plaster of the pharmacy, with alumina soap used as a thickener of lubricating oils, and with iron and chromium soaps used in dyeing and in the color printing of textiles.

As commonly known, soap is, according to its quality and the use for which it is intended, a mechanical mixture of the compound just described with varying proportions of water, with soluble alkali compounds of the rosin acids, with sal soda, $Na_3CO_210H_2O$, with sodium silicate or soluble glass, or with other inert, detersive, or odoriferous agents, incorporated for the purpose of cheapening the product, improving its appearance, increasing the detersive action, or overcoming the natural odor with an agreeable perfume. Therefore, commercial soap is a mixture of pure soap with a diluent, as water; with body-imparting substances, as talc, starch, or a petroleum residue; or with detersive agents in aqueous solution, as sodium carbonate, borax, or sodium silicate. These additions may all be present in a single soap, but the nature and amount of the additions present depend on the character of the soap itself and on the purpose for which it is intended.

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2. Classes of Soap.—There are three general classes of soap, namely, industrial, household, and toilet. In the first class are included so-called textile soaps used in the process of manufacture of cotton and woolen goods. In the second class are included the soaps that are consumed in various qualities and conditions by the laundry trade; and in the third class shaving and medicinal soaps may conveniently be included. The manufacturing of soap powder, scouring powder, and glycerine is generally associated with the soap industry.

The discussion of the subject that follows will deal with the process of manufacture rather than with the use for which the product is intended.

GENERAL OUTLINE OF THE MANUFACTURE OF A SETTLED SOAP

3. The following outline gives a general idea of the various operations performed in the manufacture of a settled laundry or domestic soap. The relation of the different operations to one another is here made clear, and the following detailed descriptions of the different operations and processes rendered more intelligible.

Source of Fatty Acids.—In the definition of a soap just given, it was stated that a soap is a salt formed by the union of an organic acid of the higher fatty series with a metal, usually an alkali metal. The acid portion of soaps is derived from various animal and vegetable fats and oils, which are compounds of the organic acids just mentioned with glycerine.

Soap Stocks.—Any fat or oil used in the manufacture of soap is called a *soap stock*, and may be of either animal or vegetable origin. The various kinds and grades of soap stock used will be fully discussed later.

Saponification.—The operation by which oils and fats are combined with the alkali metals sodium or potassium to form soaps is called *saponification*. Technically, this term has a wider meaning, and applies to any operation that brings about a separation of an organic acid from an organic base.

When an animal or a vegetable fat is boiled with a caustic alkali, a double decomposition takes place. The products are the alkali salts of the organic acids of the fats and glycerine.

Graining and Settling.—After the saponification is complete, the soap is *grained*, or brought into a somewhat granular condition, by the addition of certain salts or alkalies in whose solutions the soap is practically insoluble. When in this granular state, the soap separates from the impure liquor, or lye, which may be drained off.

Crutching.—The soap, after the preceding treatment, is introducted into a machine called a *crutcher*, where it is crutched, or stirred, until it is thoroughly mixed. Here, fillers, perfumes, etc. are introduced and incorporated into the soap.

Framing.—From the crutcher the soap is run by gravity to a rectangular box, called a *frame*, of proper dimensions, in which it is allowed to stand until it is of a consistency suitable for cutting into slabs and bars.

Slabbing.—The mass of solidified soap from the frame is first cut horizontally into slabs. This operation is called *slabbing* and is performed on a machine called a *slabber*. These slabs in turn are cut, on somewhat similar machines, into blocks of suitable dimensions for making finished cakes.

Drying, Pressing, Etc.—The rough blocks are now dried superficially until a thin skin is formed over them. They are then pressed into finished cakes in dies and wrapped and packed for shipment.

RAW MATERIALS OF SOAP MANUFACTURE

ANIMAL SOAP STOCK

4. Animal soap stock occurs on the market in a variety of grades, depending on its origin and method of preparation. This stock constitutes the chief fatty material used by the soap maker. According to the part of the animal from which it is obtained and the method of rendering, it may be classified as tallow, bone stock, and grease. These classes of animal soap stock may again occur in various grades. In determining the quality, buyers, as a rule, depend on the simple tests of color, odor, and grain, supplemented by the titer, or hardness test, which will be described later. In addition, the percentage of moisture, unsaponifiable matter and the percentage of free fatty acids are determined. The last determination is of especial importance when the stock is considered with relation to its yield of glycerine.

5. Tallow.—The tallow used in soap making varies in its composition according to the part of the animal from which it is obtained and the nature of the food used in fattening the animal. Corn-fed cattle produce the firmest fat. The fat of mast-fed cattle is not so firm as that obtained from animals fattened on oil cake. Tallow consists of stearin, olein, and palmitin.

6. The percentage of free fatty acids is not only a reliable index of the quality of the stock used by the renderer but is a telltale on the care that he has employed. The following conditions conducive to the formation of a high percentage of free fatty acids in the various grades of tallow may be enumerated:

1. Allowing the raw material to stand before rendering, especially in warm weather. After the death of the animal,

decomposition immediately sets in, and the first step in the decomposition of tallow is the separation of the fatty anhydrides from the glycerol, which is immediately followed by the decomposition of the glycerine and its loss as such.

2. An excessively high temperature in rendering tends to increase the percentage of free fatty acids. The presence of water in the tissues and the influence of the high temperature in the rendering tank tend to the hydrolysis of the glyceride.

3. Rendering in closed vessels increases the percentage of free fatty acids. It will be clear that conditions prevail here that are purposely introduced and maintained in the process for the saponification of glycerides with steam under pressure in the manufacture of fatty acids and glycerine.

4. The season of the year has a great influence on the percentage of free fatty acid in even high-grade tallows, as the table given herewith will show. These figures are taken from a whole year's consumption of the best average tallows used in a factory making a high-grade laundry soap. In determining the value of a tallow the season of the year must always be taken into consideration in respect to the free fatty acid.

Month	Lots	Free Fatty Acids Per Cent.
January	58	4.31
February	55	4.09
March	61	4.27
April	63	5.28
May	47	5.36
June	63	6.39
July	53	8.03
August	81	8.19
September	68	7.28
October	63	7.01
November	54	5.12
December	75	4.58

The significance of the free-fatty-acid determination will be fully shown when the various fats and oils are discussed

with reference to their content and yield of glycerine and the changes incident to saponification.

7. Bone Stock.—Bone stock is intermediate in quality between tallow and grease and is obtained from fresh bones by rendering in a closed vessel under pressure.

8. Grease.—The commercial term *grease* is applied to all fatty material of animal origin that cannot be classified among such distinctive products as tallow, lard, etc. It is obtained from hides, kitchen refuse, recovered garbage, offal, dead animals, etc.

White grease is made directly from hog fat and trimmings and has a large use in the manufacture of white toilet soap. Owing to its high percentage of olein it produces a soap much softer in body but with better lathering qualities. *Dark*, or *house* greases, as they are called, produce a much darker soap and are used mainly for soap powder soaps. With dark greases a boiling process and not a cold process should be employed, however, because it is necessary to remove the dark coloring matter and other impurities with the waste lyes, and also to eliminate all disagreeable odors.

MANUFACTURE OF ANIMAL SOAP STOCK

9. In the manufacture of animal soap stock the various grades of tallow are extracted from the fat-enclosing tissue that surrounds the intestines, muscles, and other organs of the animal. The feet yield neatsfoot oil. The process of rendering consists essentially in the separation of the fatty matter from the enclosing animal tissue. Tallow was originally obtained by boiling the finely divided parts of the animal containing the fat in water and skimming from the surface of the water the fat thus disengaged from the membrane. Fleshy portions of the animal previously finely chopped and rendered in the manner just mentioned yield the kettle-rendered tallow used for edible purposes. Tallow, not of packing-house origin, is usually distinguished as country or city rendered.

10. Steam Rendering.—Steam-rendered tallow is obtained by subjecting the rough fat to a steam pressure of 30 to 60 pounds per square inch in a closed vessel, such as is shown in Fig. 1. The top of the tank is on the floor level and is provided with a safety valve, a manhole *a* for introducing the rough fat, which is commonly conveyed in barrows, and a discharge pipe for the exit of fumes. Near the middle of the tank are two draw-off cocks (not shown in the figure) for the removal of the liquid tallow. Water is admitted through a valve near the bottom. At the bottom of the tank is either a large gate valve *b* or a tightly fitting door for the discharge of the "soup." The *soup*, or *soup liquor*, as it is called in the packing house, consists of soft bones, solid residuum, and water highly impregnated with albuminous matter. The liquid portion is run off and evaporated to a sirupy consistency under a partial vacuum, and is afterwards mixed with the solid matter freed from an excess of liquor by compression in a fertilizer press. This material constitutes the tankage fertilizer of the packing house.

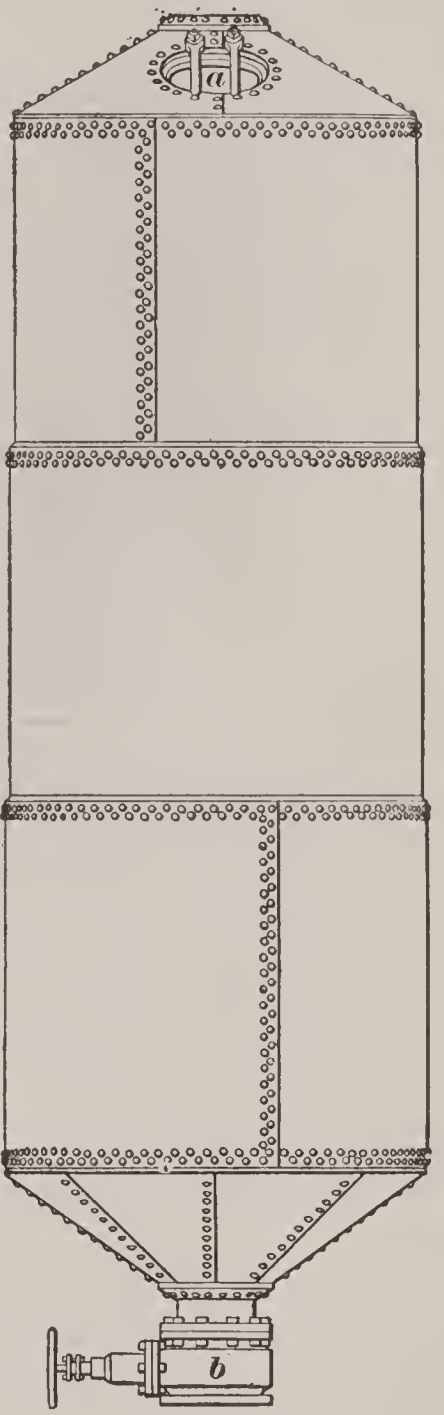

FIG. 1

After charging, these tanks, which are usually arranged in a series, are tightly closed. Water is run in, if desired, and steam is turned on. The period of working varies from 4 to 10 hours, according to the size of the tanks, the quantity of material introduced, and the steam pressure. At the expiration of the rendering period, the fat is discharged by means of the draw-off cocks. When the last portions of fat are below the level of the draw-off cocks, water is admitted into the tank

from below, and the fat floating on the surface of the water is thus completely discharged. The remaining contents of the tank is then dropped through the discharge gate at the bottom.

11. Chemical Rendering.—While most of the animal stock used in the manufacture of soap is prepared by the steam-rendering process, chemical rendering is carried on to a considerable extent. For this purpose, dilute liquors of either sulphuric acid or caustic soda are used, and the odorous substances present in the stock become partly destroyed or combined with the chemical agent used. If the acid process is employed, wooden or lead-lined tanks must be used for the operation.

VEGETABLE SOAP STOCK

12. Any vegetable oil may be employed for the manufacture of soap, its applicability for this purpose being determined by its character, cost, and the intended use of the soap made from it. Except in making soft soap or soap for special purposes vegetable oil is seldom used alone. However, oil of some character finds its way into most every soap charge. Linseed oil and the various nut oils—peanut oil, for example—cannot compete with cottonseed oil because of their greater initial cost, although in cases of very large flax crops linseed oil has been cheaper than either cottonseed or corn oil. Castor oil is used but little, its very limited consumption being confined to the manufacture of transparent soaps. Linseed oil is used extensively in Europe in the manufacture of soft soap. In the United States soft soap finds only limited sale as a detergent. The soft soaps used in the cotton and woolen industries are made from a non-drying glyceride base. In Table I is given the average percentage yield of oils of vegetable origin. The percentage yield of oil from seeds, fruits, etc. is dependent on a variety of conditions, chief among which are the character of the soil, the weather, and the degree of ripeness, and these are subject to extreme variations. These conditions influence, as well, the specific gravity of one and the same oil. Moreover, according

to the age, mode of preparation, etc., of the oil, the variations in specific gravity may be as great as the difference between the density of one oil and that of another serving as an adulterant.

13. Cottonseed Oil.—The chief product of cottonseed, which constitutes about two-thirds of the weight of the unginned cotton grown in the Southern States, is cottonseed oil. In recent years, this oil has attained great importance as a soap stock, although its use in this connection is small compared with its consumption for edible purposes. Crude cottonseed oil is a thick, reddish-brown to black oil of extremely

TABLE I

YIELD OF OIL FROM VARIOUS SEEDS, NUTS, ETC.

Seed	Percentage Yield of Oil	Seed	Percentage Yield of Oil
Castor (Indian) . .	51–53	Maize, or corn . . .	6–10
Castor (American)	46–49	Olive (pericarp) . .	40–60
Coconut	40–45	Palm (pericarp) . .	65–72
Colza, or rape	33–43	Palm kernel	45–50
Cottonseed	24–26	Peanut	43–45
Linseed	38–40	Sesame.	50–57

varying quality, depending on the season and the care exercised in the collection and storage of the seed. The crude oil contains from 10 to 15 pounds of coloring matter per ton of seed. This coloring matter has been isolated, but is of little practical value. The loss in refining the crude oil is from 5 to 7 per cent. This is an extremely varying factor, depending on the percentage of free fatty acids and the proportion of coloring and albuminous matter present, or, briefly, on the character of the seed. The yield of oil depends on the soil, season, and skill of manufacture, and ranges from 35 to 42 gallons of crude oil per ton of seed.

14. Refining of Crude Cottonseed Oil.—In the refining process, the first step is to separate as quickly and as

thoroughly as possible the foreign matter from the expressed crude oil. The residue obtained on settling or filtration is known as *settlings* or *foots*. The precipitate, or residue obtained in the refining process is sometimes termed *soap stock* but is known in the cottonseed trade as *cottonseed foots*, under which name it is sold. (*Foots* is a loose term at best, and foots and soap stock are frequently used indiscriminately.) The crude oil freed from settlings is now pumped into the first-treatment tank, where it is agitated under increased temperature with caustic-soda lye of strength and proportion adapted to the quality of oil undergoing treatment. When sufficient time has elapsed for the complete absorption of the alkali, the agitation is ceased and the contents of the kettle is allowed to remain at rest. During this time the soap, which is formed by the combination of the free fatty acids with the caustic alkali and is contaminated with the organic impurities of the oil, settles to the bottom. The supernatant oil thus partly clarified is then transferred to the second-treatment tank, where it undergoes a bleaching process with fullers' earth. The proportion of fullers' earth used varies with the quality of the oil and may run from 2 to 5 per cent.; often a second treatment with fullers' earth after filtration is required.

The oil after agitation with fullers' earth, under increased temperature, is passed through the filter press. The filtrate constitutes the prime summer yellow cottonseed oil used in soap making. The various grades of edible and industrial cottonseed oils are obtained from this product by subsequent treatments with fullers' earth and filtration. The winter cottonseed oil used in miners' lamps requires limpidity at a low temperature. This condition is obtained by chilling the oil to a temperature below 0° C., whereby the so-called cottonseed-oil *stearin*, which is really palmitin, separates. This cottonseed stearin is used in the manufacture of oleomargarine, and of butter and lard substitutes.

15. Grades of Cottonseed Oil.—The requirements of the Texas Cottonseed Crushers' Association for the various grades of cottonseed oil compel a uniformity of quality that

is absent in the soap stock of animal origin. The summer yellow oil employed in soap manufacture is usually examined for color, moisture, free fatty acids, and titer, the last test being of chief importance in determining comparative value for the use of soap makers.

16. Crude Cottonseed Oil.—The following are rules of the Texas Cottonseed Crushers' Association relating to cottonseed oil:

Measurement.—A tank (tank car) of cottonseed oil shall be 125 barrels. A barrel of oil, if sold loose, shall contain 50 gallons. A gallon of oil shall weigh $7\frac{1}{2}$ pounds, avoirdupois.

Classification.—Crude cottonseed oil shall be classed and graded as follows:

Choice crude must be made from sound decorticated seed, must be sweet in flavor and odor, light in color, free from water and settlings, and test not over 1 per cent. of free fatty acids. It shall produce, when properly refined, choice summer yellow oil at a loss in weight not exceeding 6 per cent. for Texas oil, and at a normal loss for oil from all other parts of the country.

Prime Crude.—Crude cottonseed oil to pass as *prime* must be made from sound decorticated seed, must be sweet in flavor and odor, free from water and settlings, and must produce prime summer yellow grade by the usual refining methods with a normal loss in weight, provided the oil shall not be rejected for a nominal amount of settlings; but reasonable reduction shall be made in value for all such settlings in excess of $\frac{1}{4}$ per cent.

Off Oil.—All oil neither choice nor prime shall be called *off oil*, and shall be sold by sample.

17. Refined Cottonseed Oil.—According to the rules of this association, refined cottonseed oil shall be classed and graded as follows, summer yellow oil only being considered:

Choice summer yellow must be sweet in flavor and odor, of light straw color, clear and brilliant in appearance, free from moisture, and must bleach to a choice white.

Prime summer yellow must be clear, sweet in flavor and odor, and of yellow color, not reddish, and free from water and settlings.

Off Oil.—This grade consists of all oils having any objectionable flavor or odor, or that are of a reddish color.

18. Cottonseed Oil Soap Stock.—The precipitate obtained from the crude oil freed from settlings, on treatment with caustic-soda lye, consists of soap and free oil mixed with mucilaginous and coloring matters. This mixing

undergoes further treatment with caustic alkali, which transforms all the free oil into soap. The finished soap is grained, and is then subjected to further brine and alkali washings in order to obtain a product as free from odor and light in color as possible. After this stock has been suitably purified and is on the final settling, it is run while hot and in a semifluid condition into barrels.

19. Requirements of the Texas Cottonseed Crushers' Association for Soap Stock.—According to the requirements of the Texas Cottonseed Crushers' Association, all sales, unless otherwise agreed on by buyer and seller, are on a basis of 50 per cent. of fatty acid, not to fall below 40 per cent. If containing less than 40 per cent. of fatty acid, soap stock shall not be considered merchantable. Delivery is to be made in iron-bound hardwood packages or tank cars. A tank car of soap stock shall be 50,000 pounds for contract purposes.

20. Coconut Oil.—The fruit of the coco palm, the *Cocos nucifera* of the tropics, is the source of coconut oil. The oil is expressed from the pulp of the nut, which contains about 50 per cent. of oil. It occurs on the market in three general grades, namely, Cochin, Ceylon, and copra oil. The terms *Cochin* and *Ceylon* have reference to the geographical origin of the fruit.

Considerable coconut oil is produced in the West Indies and in the tropical parts of America. That from Trinidad compares very favorably in color, body, and odor with the Cochin grade; but that from Cuba is inferior in quality and yellowish in color, and therefore cannot be used for the better grades of bath and floating soaps. Cochin coconut oil is usually sufficiently superior in quality to command a price of from $\frac{1}{2}$ to 1 cent a pound more than Ceylon oil.

Cochin coconut oil is expressed from fruit grown in Cochin-China and adjacent territory, and on the islands of the China Sea.

Malabar and Manila oil is of good quality. Mauritius and the Fiji Islands also produce considerable. The coco palm is

a native of Cuba, and at one time oil crushing was a thriving industry on that island.

Ceylon coconut oil is a product of the island of Ceylon and of the adjacent regions. The different grades of coconut oil arise from the varying skill and the nature of the apparatus employed in its recovery, some of the apparatus being very crude. Where improved milling machinery has been introduced, coconut oil of uniform and superior quality is obtained; the greater part of the oil, however, is extracted by the most primitive methods. The oil arrives at the factory in immense casks, pipes, puncheons, and hogsheads containing from 800 to 2,000 pounds.

Copra coconut oil is made from the dried pulp or meat of the coconut, called *copra*. This pulp yields, on steaming and pressing, the lowest grade of coconut oil. The best oil of this grade is obtained from the ripest and most quickly pressed copra. Owing to its high percentage of the lower fatty acids and to its greater exposure, the copra oil is more liable to become rancid than is oil of the Ceylon and Cochin grades. The Ceylon and Cochin oils are expressed in the districts near the shipping ports, while copra is produced almost entirely in territory deficient in shipping facilities. Great quantities of copra are shipped to Marseilles, France, where the oil is expressed. In Sydney, New South Wales, copra crushing is a thriving industry.

21. Coconut oil is desirable as a soap stock because it contains a high glycerine yield and possesses distinct and peculiar qualities that define it sharply from all other animal and vegetable oils. In this connection, it may be well to note that there is no sharp distinction between a fat and an oil. Fat, which is usually of animal origin, is the term generally applied to the glycerides that are solid at ordinary temperatures; oil, on the other hand, may be of either animal or vegetable origin and is liquid at ordinary temperatures.

22. Palm-Kernel Oil.—In its chemical composition and behavior toward saponifying agents, palm-kernel oil is closely allied to coconut oil. While it is used extensively in

Europe, it finds only limited application in the United States as a soap stock. It is expressed from the kernel of the palm nut, the fleshy envelope of which is the source of palm oil. The oil is white and has an agreeable odor and taste, but on aging it becomes rancid. Oudemans gives the following as the approximate composition:

Glyceride	Per Cent.
Olein	26.6
Stearin, Palmitin, Myristin	33.0
Laurin, Caprin, Caprylin, Caproin	44.4

23. Palm Oil.—The fleshy part of the fruit of the palm tree, the *Elæis Guineensis* and the *Elæis melanococca*, native along the west coast of Africa, is the source of palm oil. According to its source and the mode of expressing it, palm oil is of butter-like to tallowy consistency, varying in color from orange to dark red, and possesses a characteristic violet-like odor.

The oil can be bleached by blowing air through it for a number of hours while the oil is maintained at a temperature of 80° to 90° C. But this can be accomplished better and more quickly by chemical bleaching, which destroys the odor as well as the color.

The chemical bleaching of palm oil is carried out in the following manner: After carefully removing all water and impurities by subsidence, the oil, cooled to a temperature of 105° to 110° F., is pumped into a lead-lined tank. While being constantly agitated by air, $\frac{3}{4}$ of 1 per cent. of bichromate of soda dissolved in the least possible amount of water is run in, followed by $1\frac{1}{2}$ per cent. of hydrochloric acid and $\frac{1}{4}$ per cent. of sulphuric acid. At the end of 20 minutes the bleaching will be finished, and the acids and oxide of chromium are removed by allowing 25 per cent. of hot water to run

in. It is preferable to allow the contents of the tank to remain undisturbed over night and to remove the clear oil in the morning.

The *Lagos oil* is the best quality made; it is of a deep, reddish-orange color and contains free fatty acids averaging from 20 to 30 per cent. The common grades of palm oil are yellow in color, and on account of the primitive methods employed in extracting them, the free fatty acids are very high, running from 50 to 80 per cent. Deductions for moisture, dirt, and impurities are allowed on sales made, provided they amount to over 2 per cent., which is generally the case.

Since the titer of palm oil is very uniform, never varying much from 44° to 45° C., the chief industrial chemical tests made are the determinations of the impurities and of the free fatty acids present.

24. Corn Oil.—The germ obtained as a by-product in the manufacture of starch and glucose from maize is utilized in expressing corn oil. This oil is closely allied to cotton-seed oil in its soap-making properties. It is usually of a bright-yellow color, but may be bleached with fullers' earth to whiteness, as is done with certain edible grades of cotton-seed oil.

In the manufacture of the oil, the corn is first steeped in water, so as to loosen the hull from the grain, which becomes swollen and tough from the absorption of water. The steeped kernel is then passed between rollers to separate the envelope and the starch from the softened germ, which remains whole and of the size of a grain of rice. The crushed corn is then transferred to tanks filled with water, in which the crushed grains sink, leaving the germs to float on the surface. These are removed, cooked, and compressed for the oil.

On account of its higher titer, from 33° to 35° C., cotton-seed oil as a soap stock is much to be preferred to corn oil, the titer of whose fatty acids ranges from 17° to 19° C. Corn oil mixed with other stocks is used quite extensively in the production of soaps of soft body, to be used in the manufacture of soap powders. This mixture gives a soap readily

soluble in cold or lukewarm water, a characteristic very essential to a good powder.

25. Olive Oil.—The pulp, or fleshy portion, of the fruit of the oilve tree, the *Olea Europæa*, native in the Mediterranean countries, is used for making olive oil. In these countries, olive oil has been employed from the earliest time as the fatty base of Castile soap. The use of olive oil for this purpose has of late years been largely displaced by the cheaper cottonseed oil, large quantities of the latter being exported from the United States to Marseilles for this purpose. Olive oil is used chiefly as an edible oil, and inferior grades only are used in the soap kettle. Olive oil finds very limited use as a soap stock in the United States. It contains about 72 per cent. of olein and 28 per cent. of palmitin, and behaves like cottonseed oil toward saponifying agents.

In the manufacture of olive oil, about 10 bushels of olives is crushed at a time in an edge-stone mill. The pasty mass that results, consisting of pulp and stones, is then placed in filter cloths and subjected to hydraulic pressure. The first pressing of the olives yields the finest oil. After the first pressing, which yields the virgin oil, as it is sometimes called, the press cake is ground up with water in the edge-stone mill, and the paste is then subjected to a second pressing. The second pressing yields an oil of inferior quality. The press cake after the second pressing still contains a large quantity of oil which, when recovered, constitutes the olive-oil foots of commerce. Table II shows the specific gravity, weight per gallon, etc. of the principal fatty oils.

26. Olive-Oil Foots.—The oil remaining in the press cake after the second pressing may be extracted in either of two ways, but when recovered it is of such inferior quality as to be suitable only for industrial purposes. It is fairly fluid, dark green to black in color, and has a disagreeable odor. Its inferiority results from being contaminated by the green coloring matter and pulp of the fruit. To recover the remaining oil, the press cake is first well ground, hot water being added during the process. The dark pasty mass is

then transferred to a tank and agitated with water until the broken olive stones drop, free from pulp, to the bottom of the tank. The oily residuum floating on the surface of the water is then transferred to another tank, where the free oil is removed. The pulp residuum is again pressed and yields some oil. Olive-oil foots obtained in this manner are said to be *washed*.

The press cake may also be extracted with a volatile solvent, carbon disulphide or naptha being commonly used.

TABLE II

SPECIFIC GRAVITY OF FATTY OILS AT 15° C. (60° F.)

Name of Oil	Specific Gravity
Almond oil	.918–.919
Arachic (peanut) oil	.917–.920
Castor oil	.959–.967
Coconut oil	.924–.926
Corn oil	.921–.922
Cottonseed oil	.923–.925
Lard oil	.912–.915
Linseed oil	.932–.936
Neatsfoot oil	.914–.917
Olive oil	.916–.918
Palm oil	.943–.946
Palm-kernel oil	.9119 (at 40° C.)
Rape oil	.913–.917
Sesame oil	.924–.926
Tallow oil	.910–.912
Tallow	.943–.952

The broken press cake is agitated with the solvent, after which the solution thus obtained is transferred to a covered tank. Here the solvent is distilled off and collected for subsequent use, leaving the recovered oil behind. This oil is black and retains the odor characteristic of the solvent. It is inferior to *washed* foots. This process, however, possesses the advantage of extracting the oil completely.

Soap made from olive-oil foots retains the green color of the recovered oil; the color, however, gradually bleaches out on exposure.

27. Red Oil.—In the manufacture of candles, a by-product known as red oil is obtained. This oil consists almost wholly of oleic acid, and derives its name from the color that it acquires on aging. The color, however, is chiefly due to contact with the iron. Sometimes this color is developed by the use of dyes and sometimes by chemical treatment with sulphur or nitric oxide. Red oil occurs in two grades, namely, saponified and distilled red oil.

Saponified red oil is obtained by either acid, lime, or aqueous saponification under pressure, in specially constructed tanks called autoclaves, or digesters. The mixed fatty acids resulting from saponification are resolved roughly into stearic and oleic acids by pressure through filter cloths. The stearic acid still remaining in the liquid portion is separated by chilling, whereby the commercial oleic acid, or red oil, is obtained.

Distilled red oil is obtained by distilling the mixed fatty acids with steam. By means of the process of fractional condensation, fatty acids of different melting points are separated. Distilled red oil varies in its composition according to the method employed in its manufacture. The following are analyses of two samples of commercial oleic acid:

Ingredients	Sample A Per Cent.	Sample B Per Cent.
Color	Pale	Brown
Oleic acid	93.06	87.70
Oil	6.04	9.41
Hydrocarbons	.90	2.89
Total	100.00	100.00
Specific gravity	.897	.904
Turbid at	42° F.	38° F.

Red oil is a valuable soap stock. It admits of a nearly complete saponification with soda ash, as will be fully explained elsewhere.

28. Manufacture of Saponified Red Oil.—Saponified red oil, as just stated, may be obtained by three methods of saponification, namely: lime saponification, acid saponification, and aqueous saponification.

29. Lime-Saponification Process.—The digester, or autoclave, used in the lime-saponification process, is a strongly built tank, usually of copper, although some are made of iron, from 3 to 5 feet in diameter and from 18 to 25 feet in height. The digester may be set up either horizontally or vertically. It is covered with an asbestos jacket, to retain the heat, and is provided with a safety valve, a cock for the removal of samples, and a pressure gauge. At one end are located pipes for the introduction of the tallow and lime, for the discharge of the contents of the digester after saponification, and for the introduction of live steam.

The tallow is previously purified, if required, by boiling in weak brine and then allowing the impurities to subside. The brine wash is then run off, and the tallow is maintained in a fluid state by means of a closed steam coil. The quantity of unslaked lime commonly used for saponification is from 2 to 4 per cent. of the weight of the tallow. Both the tallow and lime tanks are on an elevation above the digester, and after the lime has been thoroughly mixed with water and the tallow melted, they are allowed to run by gravity into the digester. The charging of the digester may be hastened by creating a partial vacuum in it by the condensation of steam previous to running in the charge.

After the charge has been added, steam is turned on and maintained at a pressure of from 8 to 10 atmospheres for a period of from 4 to 10 hours, or until the saponification is complete; 8.7 per cent. of lime is theoretically required, but under the conditions maintained in the digester, from 2 to 4 per cent. has been found to be sufficient in practice. Samples are removed from time to time and tested for unsaponified matter. On completion of saponification, the contents of the disgester is blown into wooden tanks, or vats, situated above the digester.

The mass resolves itself into two layers: the supernatant lime *rock*, consisting of lime soap and fatty acids, and the *sweet* water, in which is dissolved the glycerine liberated from the stock. The glycerine solution is now allowed to flow by gravity to the glycerine plant, while the lime rock is again boiled up with water and live steam in order to remove the last traces of glycerine. This wash liquor is removed as before.

The decomposition of the lime rock is effected by adding slowly, under constant agitation, the calculated quantity of dilute sulphuric acid. The fatty acids of the lime soap are thus set free. The mass at once resolves itself into two layers: the supernatant layer, consisting of the total fatty acids, and the water containing the calcium sulphate in solution and as a precipitate. The acid liquor and precipitate are now discharged into the sewer, and the fatty acids are washed free from all traces of sulphuric acid.

30. Acid-Saponification Process.—In Fig. 2 is shown a type of apparatus of English manufacture employed in the acid-saponification process for the manufacture of fatty acids for candle stock.

The raw material, whether it be tallow, palm oil, recovered grease, or any fatty body containing stearin, is first melted in the tank marked *A* and is then transferred to the storage tanks *G*. These tanks are wooden and lead-lined and are provided with acid-resisting steam coils. In these storage tanks the fat undergoes a preliminary purification, as already briefly described. The mass is then transferred to the acidifier marked *D*. It is there treated with from 4 to 12 per cent. of concentrated sulphuric acid, which is introduced by gravity from a tank *E* located immediately above. In the acidifier *D*, the mixture is subjected to the action of superheated steam furnished by the superheater *F*. To condense the acrid vapors evolved during the reaction, a jet condenser provides a slight vacuum in the acidifier, and the vapors are thus drawn over and discharged into the reservoir *d*.

After the acidification is complete, the material is discharged into the storage tanks *G*, where the acid liquor is

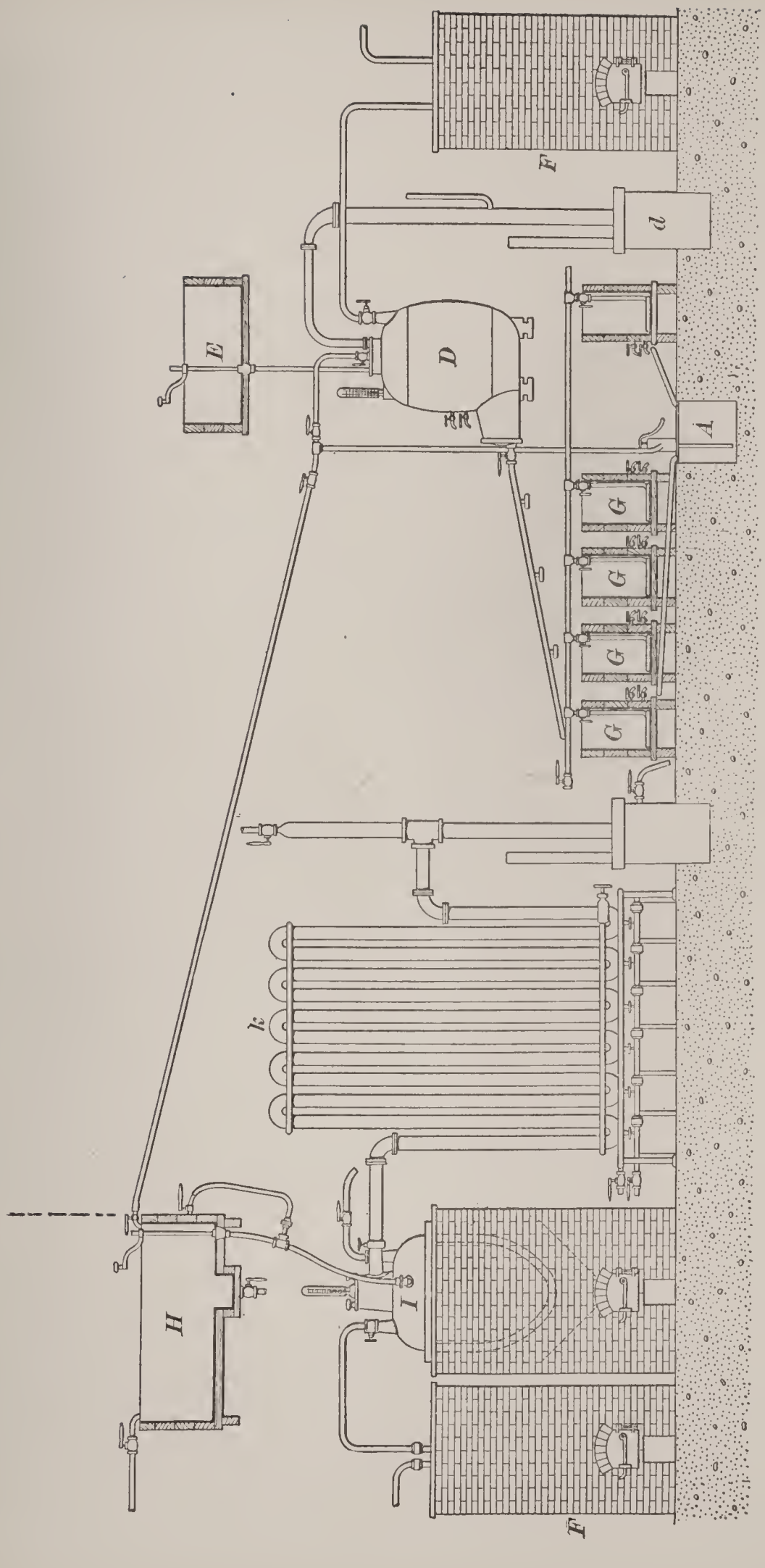

FIG. 2

removed and the fatty acids are washed free from all traces of sulphuric acid.

31. Aqueous-Saponification Process.—Many establishments manufacturing candle stock employ neither acid nor lime in the hydrolysis of the glyceride, but saponify their tallow, bone fat, or other stock merely in the presence of water and a catalyst under a steam pressure of 150 pounds. These catalysts, or *saponifiers*, are usually made by the action of sulphuric acid on a solution of oleic acid in an aromatic hydrocarbon. This hydrocarbon may be benzene, toluol, or naphthalene. Higher alcohols have also been successfully employed, such as phenol and cetyl alcohol. It can readily be seen how a sulphonated product is obtained which in the case of benzene corresponds to $C_6H_4(SO_3H)C_{18}H_{35}O_2$. It requires from 1 to $2\frac{1}{2}$ per cent. of the saponifier for the reaction, which proceeds best when the fat or oil contains a little free fatty acid of its own. This is called the autoclave process. Saponification by means of water is the simplest and most convenient of the three processes described, inasmuch as the lime and acid treatments are made unnecessary. The process otherwise is carried on in precisely the same manner as described in the lime-saponification method.

32. Twitchell Process.—A process for the separation of the fats and oils into fatty acid and glycerine has been worked out by Twitchell. This process differs from similar processes in that he employs a saponifier. This saponifier is made by allowing sulphuric acid to act on oleic acid in the pressure of an aromatic hydrocarbon, benzene or naphthalene. When benzene is used the formula for the saponifier may be expressed as $C_6H_4(SO_3H)C_{18}H_{35}O_2$.

The process requires that the original fat or oil be purified by boiling with dilute sulphuric acid. It is then mixed with an equal amount of distilled water and $1\frac{1}{2}$ to 2 per cent. of the saponifiers and boiled in wooden tanks, fitted with brass coils and a tight cover. Any access of air tends to darken the fatty acid and this has been one of its chief drawbacks.

The Twitchell product often has to be distilled to get light-colored fatty acids. It has not found great favor with the soapmakers as yet.

33. Distillation of the Fatty Acids.—The fatty acids, whether obtained by the lime, acid, or aqueous saponification, are subjected to the same process of distillation. When made of pure and fresh raw material, the resulting fatty acids are of sufficiently good color to press immediately. The dark-colored fatty acids before pressing are subjected to distillation with superheated steam. Referring to Fig. 2, the fatty acids are pumped to the charging tank *H* situated on an elevation above the still *I*, into which these acids may flow by gravity. The still, generally of copper or copper-lined, is of variable capacity. A still of ordinary size will accommodate from 16,000 to 18,000 pounds at a *run*, during which the volume of material in the still is kept constant by the addition of fatty acids from the charging tank above. As shown in Fig. 2, the still is incased in brickwork and is heated externally by fire and within by superheated steam, which passes through copper coils from the superheater *F*. The products of distillation are condensed in the vertical cooling tubes *k*, which connect at the bottom with coils immersed in warm water. The condensed fatty acids are here melted, to admit of their easy removal. The distillate is commonly collected in three fractions, namely, the first-run oil, comprising three-fourths of the total charge; the second-run oil, which is returned to the charging tank and redistilled with the next run; and the final portion, called from its color *green oil*. The residue in the still is known as *candle tar*.

34. Pressing the Fatty Acids.—The fatty acids, whether having been subjected to a previous distillation or used directly from the autoclave, are transferred to square, shallow pans, or trays, supported on shelves in the granulating room. These trays are of enameled iron and are so placed that each tray, beginning at the end, is at a higher elevation and slightly over the succeeding one. It is thus possible to

fill every pan in the series by running the melted fatty acids into the topmost, which, when full, overflows into the succeeding one, and so on until all are filled. Were the fatty acids cooled rapidly, the crystals of the fatty acids of different melting points would be so closely interlocked that the oleic acid could not be readily separated from the stearic. By allowing the mixture of fatty acids to cool slowly for a period of from 2 to 3 days in the granulating room, at a temperature of about 80° F., the stearic acid crystallizes in a menstruum of the liquid oleic acid. There is thus obtained at the expiration of this stage of the process a cake of stearic acid colored brown by the oleic acid.

The pan is now inverted on a woolen or a camel's-hair cloth, on which the cake falls. When the required number of cloths have been filled they are transferred to the hydraulic press. Each cloth with its contents is separated by an iron plate. Pressure is applied very gradually at first, whereupon the crude oleic acid, or red oil, is expressed. The oil is then conducted to storage tanks, from which it either is run to the department in which it is used or is barreled for shipment.

The first pressing separates about 50 per cent. of the oleic acid present and is done cold. The cakes thus obtained are subjected to a second pressing between hollow iron plates heated with steam. The hot pressing is effected in a horizontal hydraulic press. The stearic acid now obtained is of snowy-white appearance and very hard and brittle. It melts at 52° to 55° C. and is ready for the candle manufacturer.

35. Comparison of the Processes for the Manufacture of Fatty Acids.—The yield of solid fatty acids from tallow by lime saponification is from 44 to 48 per cent. Aqueous saponification admits of a slightly higher yield, namely, 50 per cent., from the same raw material; acid saponification yields upwards of 55 per cent. of fatty acids. It is found in practice that distilled stock yields a press cake of lower melting point than that obtained from fatty acids used directly from the autoclave. This fact taken together with the greater yield of the acid-saponification process with which

process distillation is used may be explained by the polymerizing action of the sulphuric acid on the oleic acid in the still, whereby a body is formed of sufficient firmness to resist being expelled from the press cake with the crude oleic acid, and thus remains to lower the melting point and to add to the yield.

With lime saponification, practically all the glycerine, upwards to 10 per cent., is obtained; with the acid saponification, not more than 3 per cent. is recovered. If it is desired to recover as much glycerine as is possible, in addition to the solid fatty acids, the lime saponification is preferable. If fatty acids are the sole desideratum, the distillation process is better.

36. Rosin.—The solid residue left on the distillation of crude turpentine is rosin. The rosin, or crude turpentine, exudes from the pine tree, chiefly the long-leaf yellow pine of the Southeastern Atlantic and Gulf States. This rosin is of whitish color and of semisolid consistency. A number of deep incisions are made in the trunk of the tree starting about 1 foot from the ground, and each incision, or *box* holds about a quart of the crude rosin. The number of boxes cut in each tree, depends on the size of the tree. As the season advances, the flow of rosin is increased by removing the bark and wood to the depth of 1 inch above the box. At regular intervals, the exuded rosin is collected and distilled.

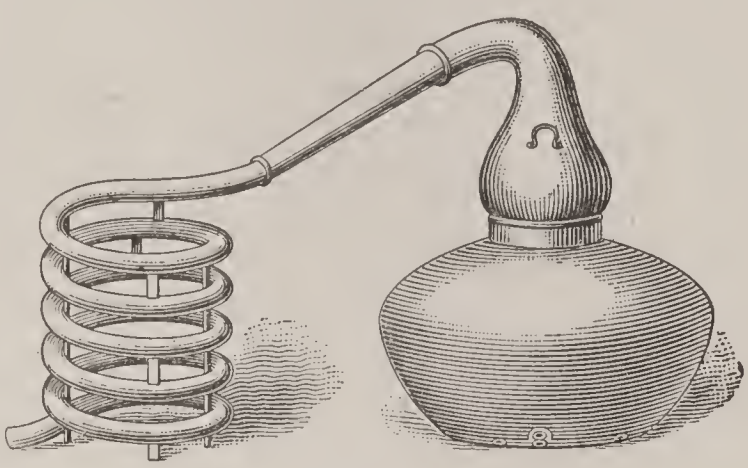

FIG. 3

The still (see Fig. 3) used for distilling rosin is made of copper and varies in capacity from 10 to 50 barrels of crude turpentine. It is mounted on brickwork and has a furnace underneath. After the still has been charged, some water is run in and the contents is heated. The fire is increased

gradually until the contents of the still has reached the boiling point, which temperature is maintained until practically all the volatile matter has been distilled over. As the distillation proceeds, water is added from time to time so as to replace that lost by evaporation and to prevent the product from being darkened by incipient burning. The distillate, separated from the water that has distilled over with it, constitutes the oil of turpentine of commerce. The hot liquid residuum in the still is now discharged through a valve near the bottom, strained through sieves of increasing mesh up to No. 80, usually three in number, and is finally run into barrels. A charge of 12 barrels of crude turpentine, weighing upwards of 4,500 pounds, will yield on distillation about 3,600 pounds of rosin and about 900 pounds of oil of turpentine.

37. The gross weight of a barrel of rosin is about 500 pounds and the net weight averages 420 pounds, the barrel itself always being paid for at the same rate as the rosin. Rosin is marketed on a basis of 280 pounds to a barrel, and according to law, the empty barrel may weigh 15 per cent. of the weight of the barrel when filled. This is equivalent to 40 pounds for Alabama and 70 pounds for Savannah cooperage.

Opaque rosins contain turpentine and water, and when used in soaps they affect the hardness to a certain extent; that is, the soaps become soft in very hot weather.

There are about fifteen grades of rosin, varying in color from *water white*, which is clear and almost colorless, to the lowest grade, commercially known as "C. A.," which is black. The various qualities arise from the length of time during which the crude rosin is collected from a single *camp*.

The first year's run furnishes the best grades, while with each succeeding year a more inferior grade is obtained. The following grades are used in the soap industry:

W. W., or Water White.
W. G., or Window Glass
N., or Extra Pale
M., or Pale.
K., or Low Pale.

Most of the rosin used for soap making is of the M and N grades.

Rosin is graded by sample, a $\frac{7}{8}$-inch cube being cut from the head of each barrel. Uniformity of size is important, as the thickness of the cube determines the shade of color, and therefore the value. Those who buy and sell rosin are provided with sample cubes representing the quality of the standard grades. The determination of the quality of a shipment, therefore, is simply a matter of comparing the sample cubes with those of the standard grades.

38. Rosin is acid in its composition, consisting of the anhydrides of the so-called rosin acids. Like red oil, rosin can be almost entirely saponified with soda ash. The alkaline salts of the rosin acids, while not constituting a true soap, possess marked detergent properties and are a valuable ingredient of household soap. The English were the first manufacturers of rosined soaps.

As rosin decreases in quality from the brighter to the darker grades, the percentage of unsaponifiable matter increases, as is indicated by the following determinations of the unsaponifiable matter:

Marks	Percentage Unsaponifiable Matter
W. W.	3.07
W. G.	3.88
N.	4.08
M.	6.34
K.	6.62

The coloring matter present in rosin is the cause of the high color of the waste soap lye withdrawn after the rosin change in the manufacture of settled rosin soap.

ALKALIES AND THEIR MANUFACTURE

39. Soda Ash, or Sodium Carbonate.—All the commercial sodium compounds start from common salt as a raw material. Before the development of the Le Blanc process, potash was used exclusively as the saponifying agent in the primitive soap manufacture of those days. The potash was obtained by burning sea-weeds and lixiviating the ashes. The solution thus obtained was then causticized with quicklime. During the embargoes of the French Revolution, the supply of potash was cut off from France. As the result of a prize offered by the French government for a practical method of manufacturing soda ash from common salt, the Le Blanc process was given to the world. So perfectly was this process outlined in its original specifications that it has undergone no change in its essential principles in its entire history.

40. The Le Blanc Process for the Manufacture of Sodium Carbonate.—The manufacture of soda ash, or sodium carbonate, Na_2CO_3, from common salt by the Le Blanc process is carried on practically in three stages, as expressed in the following reactions:

1. Common salt, or sodium chloride, is converted into sodium sulphate by treatment with sulphuric acid.

$$2NaCl+H_2SO_4=Na_2SO_4+2HCl$$

The hydrochloric-acid gas is absorbed by passing it through towers down which water is allowed to trickle. The aqueous solution of the gas thus obtained constitutes the muriatic acid of commerce.

2. The sodium sulphate obtained by the preceding reaction is mixed with coal and fused in specially constructed furnaces. The coal reduces the sulphate to sulphide.

$$Na_2SO_4+2C=Na_2S+2CO_2$$

3. The sodium sulphide is now heated with carbonate of lime, which then reacts to form calcium sulphide and sodium carbonate.

$$Na_2S+CaCO_3=CaS+Na_2CO_3$$

The product of this reaction is crude soda, or black ash. The fused mass is allowed to cool and then broken into fragments and lixiviated with water. The sodium carbonate in solution is allowed to crystallize out as $Na_2CO_3 \cdot 10H_2O$. The water of crystallization is expelled by heat, leaving the sodium carbonate or soda ash of commerce.

41. The Le Blanc process, although a creation of French ingenuity, enjoyed its greatest development on English soil, and for half a century was one of the chief mainstays of England's industrial supremacy. The practical employment of the process involved certain technical and many unsanitary disadvantages, whose baneful effects proved a constant encouragement for the development of a simpler and more hygienic process. The mechanical difficulties surrounding the production of alkali by what is now known as the *ammonia process* met their first practical solution at the hands of Ernest and Alfred Solvay, and in the past 35 years works operating the process originally covered by the Solvay patents have been established in every civilized country. The first ammonia-soda works were established in Belgium in 1863. Later, immense works were established in England by Brunner, Mond & Co., whose name is closely associated with the development of the process in Great Britain.

The Le Blanc process has received the most thorough scrutiny of the best scientific minds, and the efforts made to enable it to survive in the face of the more economical production of a competing process have resulted in the most complete economy of operation. As a remunerative producer of alkali, the ammonia process early displaced it, with the result that the process is dependent for its profits entirely on its chlorine products. As yet no economical production of bleaching powder from the calcium-chloride waste of the ammonia-soda process has been wrought out on an extensive commercial scale, and as these two rival chemical processes stand today, the Le Blanc has command of the chlorine industry, while the scepter of remunerative alkali production has passed to the ammonia process.

42. Solvay, or Ammonia-Soda, Process.—The Solvay process for the production of soda ash from common salt is based on the precipitation of sodium bicarbonate in an ammoniacal solution of common salt by means of carbonic-acid gas. Practically all soda ash now produced is obtained by this process.

In the practical operation of the Solvay process, the employment of labor is reduced to a minimum. The materials employed in the direct manufacturing processes are either in a gaseous state or in aqueous solution. The fundamental chemical reaction of the process is as follows:

$$NaCl+NH_3+H_2O+CO_2=NH_4Cl+NaHCO_3$$

The salt is dissolved in water to form a very pure and concentrated brine. It is then saturated with ammonia gas. The liquor thus formed is introduced under pressure into the *carbonating* tower at a distance about one-third from the top. The carbonating tower is upwards of 65 feet in height and is made of up of segments about 3.5 feet high and 6 feet in diameter. The carbonic-acid gas is forced into the tower through the bottom segment and is made to ascend in bubbles by means of a perforated plate covering a hole in the bottom of each segment. The reaction indicated by the preceding formula takes place in the carbonating tower. The success of the ammonia-soda process depends on the insolubility of the sodium bicarbonate in a cold, ammoniacal solution of common salt. The heat produced by the chemical reaction is taken up by cold water circulating in cooling pipes placed in each segment of the carbonating tower.

43. As the reaction proceeds, the precipitated sodium bicarbonate accumulates in the bottom of the tower, from which place it is withdrawn from time to time as a thick, milky liquid, containing ammonium chloride and sodium chloride in solution and the sodium bicarbonate in suspension. The solid bicarbonate is separated from the chlorides of ammonium and sodium in solution by means of centrifugal machines, and it is then washed with water to remove traces of these impurities. The bicarbonate is then calcined to

form a normal carbonate in accordance with the following reaction:

$$2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O$$

The Solvay soda ash thus obtained has a specific gravity of only .8, owing to its extremely finely divided condition. To increase the ease of handling this soda ash and to bring it up to the density of Le Blanc soda ash, namely, 1.2, it is made more compact by subjecting it to a second ignition. It is then ground and packed in bags and casks for shipment. Soda ash made by this process is much purer than the Le Blanc soda ash. It contains only traces of salt and bicarbonate and is free from the sulphide, sulphate, and hydrate of sodium.

44. Caustic-Soda Manufacture.—The manufacture of caustic soda is based on the following reaction:

$$Na_2CO_3 + Ca(OH)_2 = 2NaOH + CaCO_3$$
$$106 \qquad 74 \qquad 80 \qquad 100$$

According to this reaction, 100 pounds of sodium carbonate will yield on causticization 75.4 pounds of sodium hydrate. In the manufacture of caustic soda from the soda ash of the Le Blanc process, the lime is added to the solution obtained by lixiviating the black ash. The solution must not have a density in excess of 13° Baumé, or a reversion of the calcium carbonate will result. The impure solution of sodium carbonate is therefore diluted, if necessary, and the *milk of lime* added. Under heating and agitation with air, the reaction represented by the preceding formula takes place. Zinc oxide is added to reduce the sodium sulphide; thus,

$$Na_2S + ZnO + H_2O = 2NaOH + ZnS$$

The addition of sodium nitrate, together with the air used for agitation, suffices to oxidize any thiosulphate to the normal sulphate. The solution is then allowed to settle, and the supernatant solution of caustic soda is removed and evaporated until a density of 33.5° Baumé is attained, at which point most salts present as impurities crystallize out. The solution is then transferred to a heavy cast-iron pan, and the evaporation is continued over fire until all water is expelled and the caustic soda remains as a fused mass.

A sample representing the contents of the kettle is tested for total alkali. If found to be below 60 per cent. in quality, the contents is worked up to that test. If the test indicates the quality to be above 70 per cent., the product may be worked into the highest grade or into that grade testing most closely to the contents of the kettle. The reduction of quality to the grade of caustic desired is effected by the addition of salt. The fused caustic soda is then run directly into sheet-iron drums and sealed to prevent exposure to the atmosphere. Owing to the greater purity of the solutions, purer caustic soda can be more easily obtained from the Solvay process soda ash than from Le Blanc soda ash. In the case of Solvay soda ash it is not necessary to remove the impurities always characteristic of the commercial products of the Le Blanc process.

45. Although the production of caustic lye from soda ash by the soap maker may be effected at nominal cost, the use of the solid caustic, aside from other considerations peculiar to each works that may determine the installation of a causticizing plant, possesses superior advantages regarding cleanliness and convenience of working. The commercial production of solid caustic dates from 1854, at which time improvements introduced in its manufacture by William Gossage, in England, resulted in its more general use, although in a very impure state, by soap manufacturers and paper makers. Artificial alkali was first used in the manufacture of soap in 1823. It was manufactured in England by James Muspratt and according to the Le Blanc process. The Lancashire soap boilers were loath to accept this new and purer article, and it was only after Muspratt had distributed gratis scores of tons of Le Blanc soda that they became convinced of the superior economy of artificial over natural soda. The use of the sheet-iron drums was introduced by Thompson in 1857, this innovation being a most welcome improvement over cooling the liquid caustic on iron slabs and subsequently breaking it into pieces and packing in barrels for shipment.

46. Causticization of Soda Ash in the Soap Factory. The causticizing plant consists essentially of a converting

kettle, in which the chemical reaction indicated in Art. 44 is carried out, and a filter for the separation of the *lime mud*. The causticizing plant is shown in its essential characteristics in Fig. 4. It is required to causticize the soda ash as completely as possible, and for this reason the lime should be free from impurities. In causticizing a ton of soda ash, lime containing 2 per cent. of calcium sulphate will convert 42 pounds of a ton of soda ash into the less valuable product, sodium sulphate.

The solution of the soda ash in water is effected in the converting kettle *a* with the aid of live steam introduced

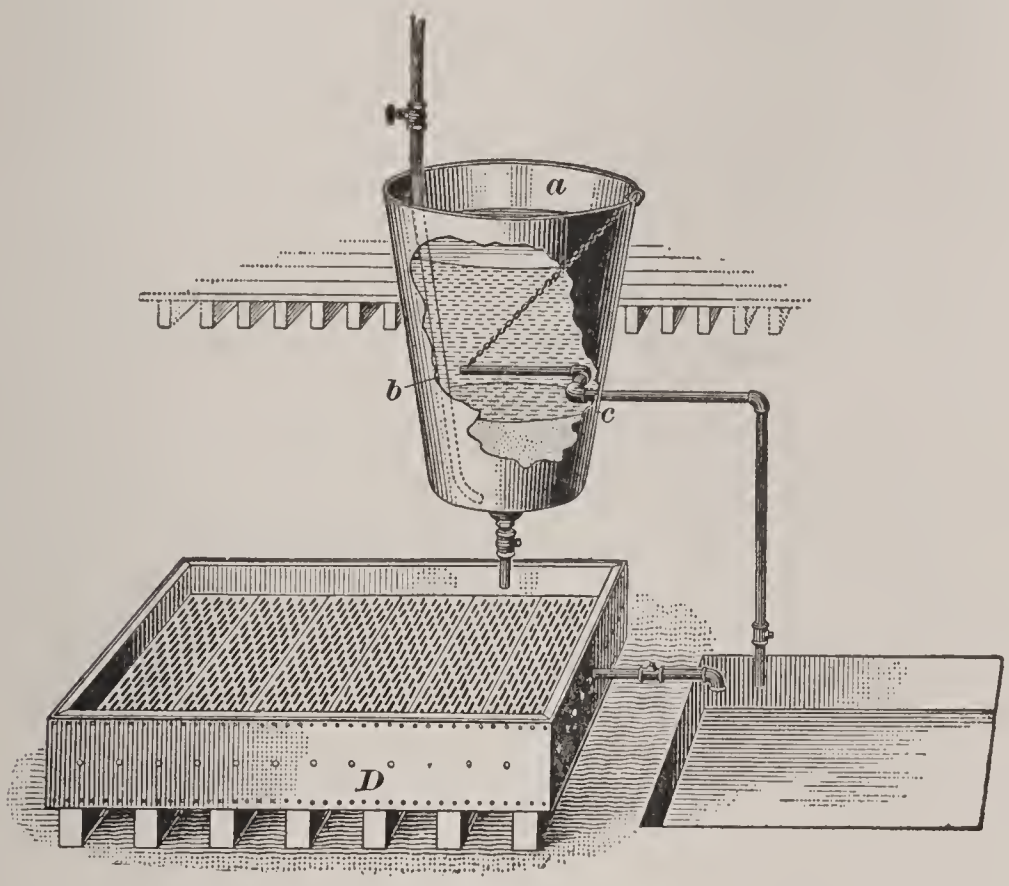

FIG. 4

through the pipe *b*, and the required amount of lime is shoveled in. The contents of the kettle is thoroughly agitated and boiled up with live steam, after which it is allowed to settle. The supernatant liquor is then pumped off through the swing-joint pipe *c*. The lime precipitate, or mud, is boiled up with water and dropped on the filter *D*, where it is drained and washed. In some instances this lime waste, known as *whiting*, is recovered. This product is utilized in the manufacture of putty and in the paper industry as a make-weight, or filler.

47. As shown by experiments carried out by Lunge, the results of which are given in Table III, the causticization is most complete with dilute solutions of soda ash.

It is claimed for the apparatus shown in Fig. 4 that a caustic-soda solution of 14.5° Baumé, equivalent to 600 pounds of 77-per-cent. caustic, can be obtained from 800 pounds of 58-per-cent. soda ash and 650 pounds of lime. As a solution of caustic soda of this density is too dilute when soap is boiled on open steam, evaporation of the weak

TABLE III

COMPLETENESS OF CAUSTICIZATION OF SOLUTIONS OF SODA ASH OF VARIOUS STRENGTHS (LUNGE)

Per Cent. Na_2CO_3 in Liquor	Specific Gravity Before Causticizing	Per Cent. Na_2CO_3 Made Caustic by Treatment	
		Test No. 1	Test No. 2
2	1.022 at 15° C.	99.4	99.3
5	1.052 at 15° C.	99.0	99.2
10	1.107 at 15° C.	97.2	97.4
12	1.127 at 15° C.	96.8	96.2
14	1.150 at 15° C.	94.5	95.4
16	1.169 at 30° C.	93.7	94.0
20	1.215 at 30° C.	90.7	91.0

caustic lye to the required density is resorted to when the facilities of the factory permit.

48. Electrolytic Production of Caustic Soda.—It has been long known that when a current of electricity is passed through a solution of sodium chloride the same is decomposed into its positive and negative ions, appearing, respectively, at the negative and positive poles, or, as they are called, the cathode and the anode.

When a solution of sodium chloride is thus electrolyzed, chlorine will appear at the anode and sodium at the cathode. Chlorine, being gaseous, will either pass into solution or be discharged into the atmosphere; sodium, being a very active

element, immediately decomposes the water surrounding the cathode, forming sodium hydrate and liberating hydrogen. Many varieties of electrolytic cells have been designed, with varying degrees of success, to serve as a commercial producer of caustic soda and chlorine. The chief mechanical difficulty in the production of a satisfactory electrolytic cell lies in the character of the diaphragm, which serves to separate the products liberated from the positive and negative poles. Chlorine must not be allowed to diffuse through the brine, as secondary reactions are set up. The problem is to find a satisfactory medium that will prevent the diffusion of the liberated products and at the same time offer no resistance to the passage of the electric current.

49. Castner Electrolytic Process for the Production of Caustic Soda and Chlorine.—In the Castner

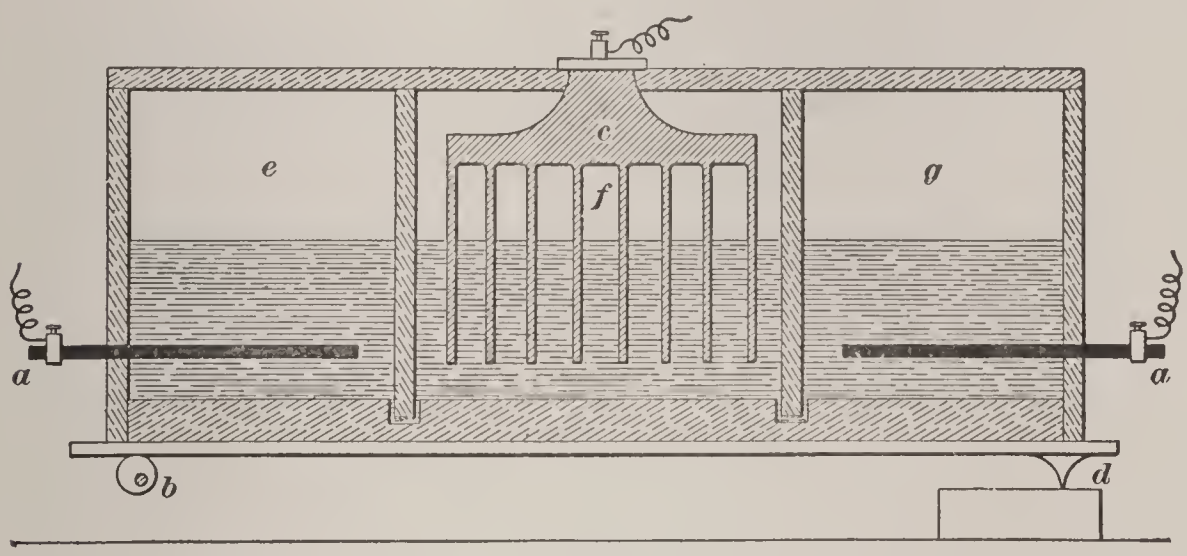

Fig. 5

cell, mercury is used to separate the chlorine liberated at the positive pole, or anode, and the sodium liberated at the negative pole, or cathode. The cell, as shown in Fig. 5, is essentially a box made of slate slabs and divided into three compartments marked *e*, *f*, *g*. Compartments *e* and *g* contain the salt solution and the carbon anodes *a*, while compartment *f* contains the caustic-soda solution and the iron cathode *c*. Sufficient mercury covers the bottom of the cell to alloy with the sodium as it is liberated. By means of the cam *b* the cell is subjected to a slight oscillation on the pivot *d*.

In this manner, the sodium-mercury amalgam is carried into compartment *f*, where the amalgam acts as the anode to the iron cathode *c*, the sodium being set free to combine with the water in compartment *f*. The electrolysis of the brine takes place in compartments *e* and *g*. The sodium immediately alloys with the mercury, which serves to carry the alkali into compartment *f*, where the formation of caustic soda takes place. A regulated supply of water is run into the middle compartment to combine with the sodium, which is allowed to flow out as a dilute caustic-soda solution in corresponding volume. The chlorine gas is removed by exhaustion from compartments *e* and *g*.

The Castner process is employed industrially at Niagara Falls for the production of caustic soda and bleaching powder, and appears to be one of the most successful devices of its kind that has yet been developed.

50. Comparison of the Methods of Alkali Manufacture.—The Le Blanc process for the manufacture of commercial alkali products is able to survive in the face of the cheaper Solvay process with its absence of waste products only by virtue of its production of hydrochloric-acid gas as a by-product.

So long as no cheaper method for the manufacture of muriatic acid is developed, the Le Blanc process will continue to be an important industry. In other respects, the Solvay process possesses every advantage.

The several electrolytic processes that have taken practical shape during the past few years have assumed a productive importance that will increase with each succeeding year. The problem of their commercial success is being gradually brought to a satisfactory solution, and what influence they may exert on the firmly established chemical processes is being watched with no little interest. As a producer of alkali, it is not likely that the ammonia process will be assailed. The older chemical process, which has so long monopolized the manufacture of bleaching powder, has most to fear from the growth of the electrolytic methods.

To sum up the essential differences between the chemical and electrolytic methods for the production of sodium compounds, it may be stated that the electrolytic process is direct, clean, labor saving, and free from worthless by-products. On the other hand, its units of plant are small, troublesome, expensive, and rapidly deteriorate with use. The chemical process provides a large output with comparatively few large units of plant of rather simple construction. The repairs, though costly, are not numerous and do not have to be applied to a vast number of small pieces of apparatus. To the disadvantage of the chemical process, it may be said to be arduous and that fairly skilled labor is required for its operation; also that a number of by-products, invariably troublesome and of little or no value, are produced.

51. Grading of Soda Ash.—The system of grading soda ash and caustic soda is based on the molecular composition of these bodies. The quotations of the various grades in terms, respectively, of 48-per-cent. alkali and 60-per-cent. caustic is handed down from the early Le Blanc days and is an evidence of the highest grades of those products they were then able to produce mechanically. The molecular weight of sodium carbonate, Na_2CO_3, is 106, composed of 62 parts by weight, or 58.49 per cent., of Na_2O, the remainder being CO_2. A soda ash that contains 58.49 per cent. of Na_2O is therefore chemically pure, this percentage being equivalent to 100 per cent. of Na_2CO_3. A 58-per-cent. alkali should contain 58 per cent. of Na_2O or its equivalent, 99.16 per cent. of Na_2CO_3; likewise, a 48 per-cent. alkali should contain 48 per cent. of Na_2O or its equivalent, 82 per cent. of Na_2CO_3. The reduction of any grade of soda to that of 48 per cent. is effected by admixture with common salt. Following are presented for comparison two fairly representative analyses of these two standard grades of soda ash:

Grade Per Cent.	Per Cent. Na_2CO_3	Per Cent. $NaCl$	Per Cent. Na_2SO_4	Per Cent. $NaOH$	$F_2O_3Al_2O_3$ SiO_2	$CaCO_3$ $MgCO_3$	H_2O
48	60.64	28.34	4.35	1.29	1.12	Traces	4.26
58	98.72	.54	.20		.10	.17	.26

52. Grading of Caustic Soda.—Caustic soda occurs on the market in a variety of grades and is sold on the basis of 60 per cent. of Na_2O. Caustic soda as a product of the alkali industry did not appear until 30 years after the industry was established in Great Britain, and the expression of its quality in the same terms as that of soda ash might therefore be expected. The molecular weight of caustic soda is 40; to arrive at sodium oxide, Na_2O, as an expression of the customary unit, 2 molecules, with a total molecular weight of 80, are used. In $2NaOH$ there are 63 parts, or 77.5 per cent. of Na_2O, the remainder being H_2O. Therefore, a chemically pure caustic soda contains 77.5 per cent. of Na_2O, or its equivalent, 100 per cent. of $NaOH$. Following is given for comparison the percentage of the essential ingredient corresponding to, but never present in, the various grades of caustic commonly found in the market:

Grade	Per Cent. $NaOH$
60	77.42
70	90.32
72	92.90
74	95.48
76	98.06
77	99.35
77.5	100.00

Sodium chloride, sodium carbonate, and sodium sulphate, in varying proportions, constitute chiefly the remainder of the ingredients. With the present system of grading based on the chemical determination of the total alkali, the Na_2O content of the Na_2CO_3 is estimated with the Na_2O in terms of which the caustic soda, or $NaOH$, is expressed. With this method of expressing the quality of the caustic soda, the soap maker has just cause for complaint in that a variable percentage of an ingredient (sodium corbonate) not so valuable as the caustic soda is included in the total percentage of the essential ingredient present. The following is an industrial analysis of a sample of commercial caustic purporting to be of 74-per-cent. quality:

	Per Cent.
Total alkali, Na_2O	74.18
Total alkali, present as $NaOH$	69.88
Caustic alkali, $NaOH$	90.18
Combined alkali, Na_2CO_3	7.35
Sodium chloride, $NaCl$	2.02

This analysis indicates the sample to be of substantially 70-per-cent. quality. The difference between the sodium hydroxide actually present and that claimed, namely, 4.30 per cent. Na_2O, is due to the 7.35 per cent. of Na_2CO_3, this being estimated as its equivalent, 4.30 per cent. of Na_2O, in the total sodium oxide. As more or less carbonate is invariably present in all commercial caustic, especially in the lower grades, the system of including it in the expression of the quality of this product is open to severe criticism. Quotations of quality are thus confessedly a misrepresentation. The only rational method is the expression of the Na_2O as free caustic, or preferably units of $NaOH$.

This would be an absolute index of the value of the caustic as a saponifying agent, and not, as by the method in vogue, an uncertain approximation of the same. English degrees indicate the strength of the ash or the caustic in terms of Na_2O, but owing to an error in atomic weights, English analyses indicate a greater percentage of Na_2O than is present. This error has become so firmly established by tradition that modern ideas have been unable as yet to eliminate it. In Germany and Russia the strength is expressed in terms of sodium carbonate. This system is perfectly rational when applied to soda ash, but is inconsistent when applied to caustic. The expression of the value of commercial caustic soda in terms of an impurity is certainly not conducive to clear ideas on the subject, even though, in so far as the soap industry is concerned, this impurity is positively worthless as a saponifying agent for neutral glycerides.

53. The superior advantages and the economy of high-grade caustic need no argument. It is true of this product that the best, within certain limits, is the cheapest. The

variation in price arises from the slight differences in cost of production of the lower grades, combined, for those grades, with the proportionally greater cost of packages, transportation, etc.

The total charges contingent on marketing a 60-per-cent. caustic are the same as those of a 70-per-cent., although the former contains considerably less of the essential ingredient; also, the cost of production of a 70-per-cent. caustic is but little more than that of a 60-per-cent. The increased cost of production of the higher grades, namely, 74 per cent. and 76 per cent., makes necessary a higher price, which is less than it would be if cost of marketing were correspondingly increased.

54. Preparation of Caustic-Soda Lye.—The solid caustic soda is delivered at the works in the familiar sheet-iron drums, containing usually about 675 pounds. The dissolving of the solid caustic is a simple operation. The method employed in effecting solution, the arrangement of the tanks, and the system of transferring the lye, vary with each establishment.

The work of solution is facilitated by inserting a false bottom or cage in the bottom of the solution tank. The usual practice is to make a strong lye of 36°–40° Baumé, and dilute as needed. To make this strong lye the proper amount of water is run into the tank. The caustic soda in drums is rolled up to the tank, the plates on the heads are cut off and about twenty slashes with an axe made into the drum along its length. The drums are then lowered to the cage. The main draw-off cock is placed about 4 inches above the bottom of the tank so that the mud is not drawn when the lye is used. By making the solution in the afternoon it will be ready for use in the morning. At that time, the drums are taken out, examined for undissolved caustic, washed, and broken up for sale as scrap.

With this arrangement, a natural circulation of liquor of different densities is set up, with the result that weak liquor continually rises to the surface, while the saturated liquor,

by virtue of its greater density, goes to the bottom. This eliminates the mechanical agitation that is necessary when the solid caustic is allowed to rest on the bottom of the tank.

TABLE IV

PERCENTAGE OF SODIUM HYDRATE, *NaOH*, IN LYES OF DIFFERENT DENSITIES, MADE FROM CAUSTIC OF VARIOUS GRADES

Specific Gravity	Degrees Baumé	77½% *%NaOH*	76% *%NaOH*	74% *%NaOH*
1.075	10	6.55	6.42	6.25
1.091	12	8.00	7.84	7.63
1.116	15	10.06	9.86	9.60
1.142	18	12.64	12.40	12.07
1.162	20	14.37	14.09	13.72
1.180	22	15.91	15.61	15.19
1.210	25	18.58	18.23	17.74
1.241	28	21.42	20.99	20.44
1.263	30	23.67	23.21	22.60
1.320	35	28.83	28.28	27.53
Specific Gravity	Degrees Baumé	72% *%NaOH*	70% *%NaOH*	60% *%NaOH*
1.075	10	6.08	5.91	5.06
1.091	12	7.43	7.22	6.19
1.116	15	9.34	9.08	7.78
1.142	18	11.74	11.41	9.78
1.162	20	13.35	12.97	11.12
1.180	22	14.78	14.36	12.31
1 210	25	17.27	16.78	14.38
1.241	28	19.89	19.33	16.57
1.263	30	21.99	21.37	18.32
1.320	35	26.79	26.04	22.31

55. In the preparation of caustic lyes of different densities from various grades of caustic, the effect of the

TABLE V—SPECIFIC GRAVITY OF CAUSTIC-SODA SOLUTIONS AT 15° C. (LUNGE)

Specific Gravity	Degrees Baumé	Degrees Twaddell	Per Cent. Na_2O	Per Cent. $NaOH$	1 Cubic Meter Contains Kilograms	
					Na_2O	$NaOH$
1.007	1	1.4	0.47	0.61	4	6
1.014	2	2.8	0.93	1.20	9	12
1.022	3	4.4	1.55	2.00	16	21
1.029	4	5.8	2.10	2.71	22	28
1.036	5	7.2	2.60	3.35	27	35
1.045	6	9.0	3.10	4.00	32	42
1.052	7	10.4	3.60	4.64	38	49
1.060	8	12.0	4.10	5.29	43	56
1.067	9	13.4	4.55	5.87	49	63
1.075	10	15.0	5.08	6.55	55	70
1.083	11	16.6	5.67	7.31	61	79
1.091	12	18.2	6.20	8.00	68	87
1.100	13	20.0	6.73	8.68	74	95
1.108	14	21.6	7.30	9.42	81	104
1.116	15	23.2	7.80	10.06	87	112
1.125	16	25.0	8.50	10.97	96	123
1.134	17	26.8	9.18	11.84	104	134
1.142	18	28.4	9.80	12.64	112	144
1.152	19	30.4	10.50	13.55	121	156
1.162	20	32.4	11.14	14.37	129	167
1.171	21	34.2	11.73	15.13	137	177
1.180	22	36.0	12.33	15.91	146	188
1.190	23	38.0	13.00	16.77	155	200
1.200	24	40.0	13.70	17.67	164	212
1.210	25	42.0	14.40	18.58	174	225
1.220	26	44.0	15.18	19.58	185	239
1.231	27	46.2	15.96	20.59	196	253
1.241	28	48.2	16.76	21.42	208	266
1.252	29	50.4	17.55	22.64	220	283
1.263	30	52.6	18.35	23.67	232	299
1.274	31	54.8	19.23	24.81	245	316
1.285	32	57.0	20.00	25.80	257	332
1.297	33	59.4	20.80	26.83	270	348
1.308	34	61.6	21.55	27.80	282	364
1.320	35	64.0	22.35	28.83	295	381
1.332	36	66.4	23.20	29.93	309	399
1.345	37	69.0	24.20	31.22	326	420
1.357	38	71.4	25.17	32.47	342	441
1.370	39	74.0	26.12	33.69	359	462
1.383	40	76.6	27.10	34.96	375	483
1.397	41	79.4	28.10	36.25	392	506
1.410	42	82.0	29.05	37.47	410	528
1.424	43	84.8	30.08	38.80	428	553
1.438	44	87.6	31.00	39.99	446	575
1.453	45	90.6	32.10	41.41	466	602
1.468	46	93.6	33.20	42.83	487	629
1.483	47	96.6	34.40	44.38	510	658
1.498	48	99.6	35.70	46.15	535	691
1.514	49	102.8	36.90	47.60	559	721
1.530	50	106.0	38.00	49.02	581	750

impurities, chiefly sodium chloride, sodium carbonate, and sodium sulphate, is to reduce the active value of the solution for the specific gravity indicated. This reduction in saponifying power is least for the highest grades and greatest for the lowest, as a natural result of the increased percentage of these impurities present. There is arranged in Table IV the percentage of sodium hydrate present in lyes of different densities, made from the usual grades of caustics, corresponding to the densities of lye made from chemically pure caustic. It is assumed that the total alkali which never actually occurs, is present entirely as caustic. The figures stated, for reasons previously given, are slightly higher than would be found in practice. However, this table possesses some value as a basis of comparison, and for many technical purposes the figures are suficiently accurate.

In the preparation of caustic-soda lye in the kettle room, the number of drums of caustic soda and the quantity of water required to furnish a lye of a certain density will be learned by experience. In Table V are given the densities of caustic-soda solutions made from chemically pure caustic soda.

56. Use of Caustic-Soda Lye.—The caustic-soda lye tank is usually situated in the kettle or soap-boiling room with an elevation of 3 or 4 feet above the tops of the kettles. It is placed at one end and piped to reach each kettle. The piping is arranged with stop valves so as not to interfere with any other boiling. Below the discharge cock, a water line is connected directly into the lye line running to the kettles. This makes it possible to deliver lye of any strength by controlling the lye and water valves. The soap boiler is provided with a Baumé hydrometer and draws the lye for test at the kettle into a cylinder or hydrometer jar as it is being delivered. A very good form of jar can be made from short pieces of pipe and fittings as shown in Fig. 6, wherein *a* may be regarded as a handle. When taking a sample the jar proper, *b*, is completely filled to *c* and the hydrometer dropped in, and the reading taken. By this means the lye is kept at the strength desired and is at all times under complete control.

57. Caustic Potash.—Potash, or crude potassium carbonate, was originally obtained from the ashes of seaweeds, and before the development of the Le Blanc process it provided the only saponifying agent then available. Later, wood ashes, beet-sugar residues, and wool scourings formed the chief commercial source. The various potassium salts are now obtained chiefly from the mineral carnallite, which is composed of the chlorides of potassium and magnesium with water of crystallization. Carnallite, with other minerals composed of chlorides and sulphates of the alkali and alkaline earth metals, occurs in immense deposits near Stassfurt, Germany.

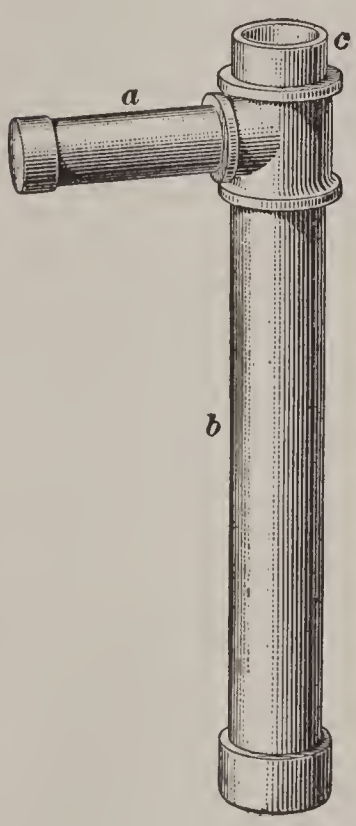

FIG. 6

Caustic potash is manufactured from carnallite by the Le Blanc process. The potassium chloride is converted into potassium sulphate by treatment with sulphuric acid. A mixture is then obtained that is analogous to the crude Glauber's salt of the Le Blanc process. This mixture is fused with limestone and coal, and the resulting mass lixiviated with water. The solution of potassium carbonate thus obtained is causticized with lime, and a solution of caustic potash results. This caustic liquor is removed, evaporated to dryness, and fused. While molten it is run into drums and comes into commerce as caustic potash. It is not so uniform in its composition as the corresponding sodium compound. Commercial caustic potash is a mixture of the following substances:

	PER CENT.
Carbonate and hydrate of potassium	80 to 95
Chlorides of sodium and potassium	5 to 10
Sulphate of potassium	5 to 15
Insoluble matter	1.5 to 3

A good caustic potash is generally opaque and of a dull-gray slate or bluish color, often streaked with red or greenish stains. It has a powerful affinity for moisture, and on expo-

TABLE VI—SPECIFIC GRAVITY OF SOLUTION OF CAUSTIC POTASH AT 15° C. (LUNGE)

Specific Gravity	Degrees Baumé	Degrees Twaddell	Per Cent. K_2O	Per Cent. KOH	1 Cubic Meter Contains Kilograms	
					K_2O	KOH
1.007	1	1.4	.7	.9	7	9
1.014	2	2.8	1.4	1.7	14	17
1.022	3	4.4	2.2	2.6	22	26
1.029	4	5.8	2.9	3.5	30	36
1.037	5	7.4	3.8	4.5	39	46
1.045	6	9.0	4.7	5.6	49	58
1.052	7	10.4	5.4	6.4	57	67
1.060	8	12.0	6.2	7.4	66	78
1.067	9	13.4	6.9	8.2	74	88
1.075	10	15.0	7.7	9.2	83	99
1.083	11	16.6	8.5	10.1	92	109
1.091	12	18.2	9.2	10.9	100	119
1.100	13	20.0	10.1	12.0	111	132
1.108	14	21.6	10.8	12.9	119	143
1.116	15	23.2	11.6	13.8	129	153
1.125	16	25.0	12.4	14.8	140	167
1.134	17	26.8	13.2	15.7	150	178
1.142	18	28.4	13.9	16.5	159	188
1.152	19	30.4	14.8	17.6	170	203
1.162	20	32.4	15.6	18.6	181	216
1.171	21	34.2	16.4	19.5	192	228
1.180	22	36.0	17.2	20.5	203	242
1.190	23	38.0	18.0	21.4	214	255
1.200	24	40.0	18.8	22.4	226	269
1.210	25	42.0	19.6	23.3	237	282
1.220	26	44.0	20.3	24.2	248	295
1.231	27	46.2	21.1	25.1	260	309
1.241	28	48.2	21.9	26.1	272	324
1.252	29	50.4	22.7	27.0	284	338
1.263	30	52.6	23.5	28.0	297	353
1.274	31	54.8	24.2	28.9	308	368
1.285	32	57.0	25.0	29.8	321	385
1.297	33	59.4	25.8	30.7	335	398
1.308	34	61.6	26.7	31.8	349	416
1.320	35	64.0	27.5	32.7	363	432
1.332	36	66.4	28.3	33.7	377	449
1.345	37	69.0	29.3	34.9	394	469
1.357	38	71.4	30.2	35.9	410	487
1.370	39	74.0	31.0	36.9	425	506
1.383	40	76.6	31.8	37.8	440	522
1.397	41	79.4	32.7	38.9	457	543
1.410	42	82.0	33.5	39.9	472	563
1.424	43	84.8	34.4	40.9	490	582
1.438	44	87.6	35.4	42.1	509	605
1.453	45	90.6	36.5	43.4	530	631
1.468	46	93.6	37.5	44.6	549	655
1.483	47	96.6	38.5	45.8	571	679
1.498	48	99.6	39.6	47.1	593	706
1.514	49	102.8	40.6	48.3	615	731
1.530	50	106.0	41.5	49.4	635	756

sure to the air, it deliquesces rapidly and soon becomes pasty. Sometimes, it presents a whitish appearance in the center of the drum, and occasionally it is honeycombed. That which contains a large porportion of salts is usually crystaline and very compact. Its high cost militates against its more general use as a saponifying agent; and it is used very little today in soap manufacture. On exposure to the air, its solutions rapidly absorb carbon dioxide, with the formation of the acid carbonate. As a chemical agent it is more active than caustic soda. Caustic potash improves the quality of all soaps of which it is an ingredient. It cannot be used in settled soap manufacture with sodium chloride as the graining agent, because an interchange of alkalies would take place and much of the potassium would be lost as the chloride. Soaps containing it are milder in their detersive action, will stand more filling without efflorescence, and possess a tougher texture.

FIG. 7

By virtue of their milder detersive action on animal and vegetable fibers, potash soaps—usually soft soaps—find wide application in the textile industry.

In Table VI is given the specific gravity of solutions of caustic potash at 15° C., according to Lunge.

MEASUREMENT OF THE DENSITY OF LIQUIDS

58. The **specific gravity** of a liquid or solid is the expression of the relation between the weight of the liquid or solid and the weight of an equal volume of pure water at a definite temperature, usually 15° C. The most convenient and practical means of ascertaining the strength of solutions of carbonated and caustic alkalies is to determine their specific gravity with a hydrometer. As shown in Fig. 7, the hydrometer is simply a closed tube with a bulb blown in one end, containing a paper scale and filled with shot or murcury. When placed in a liquid, the weighted bulb enables the hydrometer to float in an upright position. The Baumé and Twaddell hydrometers are the instruments most commonly used, the Baumé

hydrometer in America and the Twaddell hydrometer in England.

With the latter instrument, the density of pure distilled water is represented by zero, and the scale is graduated in such a manner that the specific gravity of the liquid may be cal-

TABLE VII

SPECIFIC GRAVITY AND DEGREES BAUMÉ (AMERICAN STANDARD) FOR LIQUIDS HEAVIER THAN WATER AT 60° F. (OLSEN)

Degrees Baumé	Specific Gravity	Degrees Baumé	Specific Gravity	Degrees Baumé	Specific Gravity
0	1.0000	24	1.1983	48	1.4948
1	1.0069	25	1.2083	49	1.5104
2	1.0140	26	1.2185	50	1.5263
3	1.0211	27	1.2288	51	1.5426
4	1.0284	28	1.2393	52	1.5591
5	1.0357	29	1.2500	53	1.5761
6	1.0432	30	1.2609	54	1.5934
7	1.0507	31	1.2719	55	1.6111
8	1.0584	32	1.2832	56	1.6292
9	1.0662	33	1.2946	57	1.6477
10	1.0741	34	1.3063	58	1.6667
11	1.0821	35	1.3182	59	1.6860
12	1.0902	36	1.3303	60	1.7059
13	1.0985	37	1.3426	61	1.7262
14	1.1069	38	1.3551	62	1.7470
15	1.1154	39	1.3679	63	1.7683
16	1.1240	40	1.3810	64	1.7901
17	1.1328	41	1.3942	65	1.8125
18	1.1417	42	1.4078	66	1.8354
19	1.1508	43	1.4216	67	1.8590
20	1.1600	44	1.4356	68	1.8831
21	1.1694	45	1.4500	69	1.9079
22	1.1789	46	1.4646	70	1.9333
23	1.1885	47	1.4796		

culated by multiplying the number of degrees registered on the scale by .005 and adding the product to 1; thus, the density of a liquid indicating 100° Twaddell would be $100 \times .005 + 1.000$, or 1.500. The Twaddell hydrometer is a direct-reading instrument. This means that the reading on the

scale shows the specific gravity of the liquid directly as compared with pure water at the definite temperature.

The Baumé hydrometer is adapted for the determination of the specific gravity of liquids, either heavier or lighter than water (see Tables VII and VIII). The scale used is arbitrary

TABLE VIII

SPECIFIC GRAVITY AND DEGREES BAUMÉ FOR LIQUIDS LIGHTER THAN WATER AT 60° F. (OLSEN)

Degrees Baumé	Specific Gravity	Degrees Baumé	Specific Gravity	Degrees Baumé	Specific Gravity
10	1.0000	34	.8537	58	.7447
11	.9929	35	.8485	59	.7407
12	.9859	36	.8434	60	.7368
13	.9790	37	.8383	61	.7330
14	.9722	38	.8333	62	.7292
15	.9655	39	.8284	63	.7254
16	.9589	40	.8235	64	.7216
17	.9524	41	.8187	65	.7179
18	.9459	42	.8140	66	.7143
19	.9396	43	.8092	67	.7107
20	.9333	44	.8046	68	.7071
21	.9272	45	.8000	69	.7035
22	.9211	46	.7955	70	.7000
23	.9150	47	.7910	71	.6965
24	.9091	48	.7865	72	6931
25	.9032	49	.7821	73	.6897
26	.8974	50	.7778	74	.6863
27	.8917	51	.7735	75	.6829
28	.8861	52	.7692	76	.6796
29	.8805	53	.7650	77	.6763
30	.8750	54	.7609	78	.6731
31	.8696	55	.7568	79	.6699
32	.8642	56	.7527	80	.6667
33	.8589	57	.7487		

and bears no direct relation to the specific gravity; hence, the conversion of the readings into the corresponding specific gravity is done by reference to tables prepared for this purpose. In Table IX are given the values of specific gravity corresponding to degrees Twaddell and degrees Baumé.

TABLE IX

SPECIFIC GRAVITY, DEGREES TWADDELL, AND DEGREES BAUMÉ

Twaddell	Degrees Baumé	Specific Gravity	Degrees Twaddell	Degrees Baumé	Specific Gravity	Degrees Twaddell	Degrees Baumé	Specific Gravity	Degrees Twaddell	Degrees Baumé	Specific Gravity
0	.0	1.000	44	26.2	1.220	88	44.3	1.440	132	57.7	1.660
1	.7	1.005	45	26.6	1.225	89	44.7	1.445	133	57.9	1.665
2	1.4	1.010	46	27.1	1.230	90	45.0	1.450	134	58.2	1.670
3	2.1	1.015	47	27.6	1.235	91	45.3	1.455	135	58.4	1.675
4	2.8	1.020	48	28.1	1.240	92	45.7	1.460	136	58.7	1.680
5	3.5	1.025	49	28.5	1.245	93	46.0	1.465	137	58.9	1.685
6	4.2	1.030	50	29.0	1.250	94	46.4	1.470	138	59.2	1.690
7	4.9	1.035	51	29.5	1.255	95	46.7	1.475	139	59.5	1.695
8	5.6	1.040	52	29.9	1.260	96	47.0	1.480	140	59.7	1.700
9	6.2	1.045	53	30.4	1.265	97	47.4	1.485	141	60.0	1.705
10	6.9	1.050	54	30.8	1.270	98	47.7	1.490	142	60.2	1.710
11	7.6	1.055	55	31.3	1.275	99	48.0	1.495	143	60.5	1.715
12	8.2	1.060	56	31.7	1.280	100	48.4	1.500	144	60.7	1.720
13	8.8	1.065	57	32.2	1.285	101	48.7	1.505	145	60.9	1.725
14	9.5	1.070	58	32.6	1.290	102	49.0	1.510	146	61.2	1.730
15	10.1	1.075	59	33.0	1.295	103	49.3	1.515	147	61.4	1.735
16	10.7	1.080	60	33.5	1.300	104	49.6	1.520	148	61.7	1.740
17	11.4	1.085	61	33.9	1.305	105	49.9	1.525	149	61.9	1.745
18	12.0	1.090	62	34.3	1.310	106	50.2	1.530	150	62.4	1.750
19	12.6	1.095	63	34.7	1.315	107	50.6	1.535	151	62.6	1.755
20	13.2	1.100	64	35.1	1.320	108	50.8	1.540	152	62.8	1.760
21	13.8	1.105	65	35.6	1.325	109	51.2	1.545	153	63.1	1.765
22	14.4	1.110	66	36.0	1.330	110	51.5	1.550	154	63.3	1.770
23	15.0	1.115	67	36.4	1.335	111	51.8	1.555	155	63.5	1.775
24	15.5	1.120	68	36.8	1.340	112	52.1	1.560	156	63.8	1.780
25	16.1	1.125	69	37.2	1.345	113	52.3	1.565	157	64.0	1.785
26	16.7	1.130	70	37.6	1.350	114	52.6	1.570	158	64.2	1.790
27	17.2	1.135	71	38.0	1.355	115	52.9	1.575	159	64.4	1.795
28	17.8	1.140	72	38.4	1.360	116	53.2	1.580	160	64.7	1.800
29	18.4	1.145	73	38.8	1.365	117	53.5	1.585	161	64.9	1.805
30	18.9	1.150	74	39.2	1.370	118	53.8	1.590	162	65.1	1.810
31	19.5	1.155	75	39.5	1.375	119	54.1	1.595	163	65.2	1.815
32	20.0	1.160	76	39.9	1.380	120	54.3	1.600	164	65.3	1.820
33	20.5	1.165	77	40.3	1.385	121	54.7	1.605	165	65.5	1.825
34	21.1	1.170	78	40.7	1.390	122	54.9	1.610	166	65.7	1.830
35	21.6	1.175	79	41.1	1.395	123	55.2	1.615	167	66.0	1.835
36	22.1	1.180	80	41.5	1.400	124	55.5	1.620	168	66.2	1.840
37	22.6	1.185	81	41.8	1.405	125	55.8	1.625	169	66.4	1.845
38	23.2	1.190	82	42.2	1.410	126	56.0	1.630	170	66.7	1.850
39	23.7	1.195	83	42.5	1.415	127	56.3	1.635	171	66.9	1.855
40	24.2	1.200	84	42.9	1.420	128	56.6	1.640	172	67.0	1.860
41	24.7	1.205	85	43.2	1.425	129	56.9	1.645	173	67.5	1.865
42	25.2	1.210	86	43.6	1.430	130	57.1	1.650			
43	25.7	1.215	87	44.0	1.435	131	57.4	1.655			

CHEMISTRY OF SOAP MANUFACTURE

59. In the preceding examination of the raw materials of soap manufacture there have been considered those bodies which carry the two compounds—namely, a glyceride and a caustic alkali—that, when in chemical combination, form soap. Soap boiling, therefore, consists essentially in bringing a fatty body and a caustic alkali in aqueous solution in contact under suitable conditions, whereby a simple chemical reaction takes place with the formation of an alkaline salt of a fatty acid and the liberation of glycerine. This reaction is known as *saponification.*

60. For the purpose of explanation, the fatty body will be represented by 1 molecule of stearin and the saponifying agent by 3 molecules of caustic soda; thus:

$$\underset{\text{stearin}}{C_3H_5(C_{18}H_{35},O_2)_3} + \underset{\text{caustic soda}}{3NaOH} = \underset{\text{glycerine}}{C_3H_5(OH)_3} + \underset{\text{sodium stearate}}{3C_{18}H_{35}O_2Na}$$

The term saponification is also applicable to a vast number of similar chemical changes in which an alcohol is set free and an acid is produced, when water is the saponifying agent, or an alkaline salt of the fatty acid, that is, soap, when the saponifying agent is an alkali.

GLYCERIDES AND THEIR PROPERTIES

61. In order to understand thoroughly the soap-making properties of the various fats and oils and their behavior in the soap kettle, it is necessary to be familiar with the chemical properties of the various glycerides that constitute the fats and oils employed in soap manufacture. The variation in the amount of alkali absorbed by any particular fat or oil arises from differences in the composition of the glycerides themselves and from the varying proportions in which the glycerides occur in any particular stock. It is a well known fact that fats and oils are indefinite mixtures of various glycerides, and that the amount of alkali absorbed is influenced by the nature of the glycerides characteristic of the stock.

TABLE X

ACIDS OF THE ACETIC SERIES—GENERAL FORMULA, $C_nH_{2n+1}COOH$

Acid	Formula	Mol. Wt.	Corresponding Glyceride	Formula	Mol. Wt.	Per Cent. of *NaOH* Absorbed	Per Cent. of Glycerine Set Free	Per Cent. of Fatty Acids Set Free	Natural Source
Formic	$H{\cdot}COOH$	46	Formin	$C_3H_5(O{\cdot}HCO)_3$	176	68.19	52.28	78.41	The acid occurs in bodies of ants, in the stinging pine, and in certain nettles
Acetic	$CH_3{\cdot}COOH$	60	Acetin	$C_3H_5(O{\cdot}CH_3CO)_3$	218	55.04	42.20	82.56	Occurs naturally only in slight quantities in oil of *Euonymus Europæus.*
Propionic	$C_2H_5{\cdot}COOH$	74	Propionin	$C_3H_5(O{\cdot}C_2H_5CO)_3$	260	46.15	35.38	85.38	Occurs in small quantities in the fruit of Gingko biloba.
Butyric	$C_3H_7{\cdot}COOH$	88	Butyrin	$C_3H_5(O{\cdot}C_3H_7CO)_3$	302	39.74	30.47	87.42	Cow's butter.
Valeric	$C_4H_9{\cdot}COOH$	102	Valerin	$C_3H_5(O{\cdot}C_4H_9CO)_3$	344	34.88	26.74	88.94	The acid occurs in the animal and vegetable kingdoms, free, and as an ester.
Caproic	$C_5H_{11}{\cdot}COOH$	116	Caproin	$C_3H_5(O{\cdot}C_5H_{11}CO)_3$	386	31.09	23.83	90.16	Cow's butter, coconut, and palm-kernel oils.
Oenanthylic	$C_6H_{13}{\cdot}COOH$	130	Oenanthylin	$C_3H_5(O{\cdot}C_6H_{13}CO)_3$	428	28.04	21.50	91.14	Occurs in small quantities in Kalmus oil.
Caprylic	$C_7H_{15}{\cdot}COOH$	144	Caprylin	$C_3H_5(O{\cdot}C_7H_{15}CO)_3$	470	25.54	19.57	91.91	Cow's butter, coconut, and palm-kernel oils.
Pelargonic	$C_8H_{17}{\cdot}COOH$	158	Pelargonin	$C_3H_5(O{\cdot}C_8H_{17}CO)_3$	512	23.44	17.97	92.58	The acid occurs naturally in leaves of *Pelargonium roseum.*
Capric	$C_9H_{19}{\cdot}COOH$	172	Caprin	$C_3H_5(O{\cdot}C_9H_{19}CO)_3$	554	21.66	16.61	93.13	Cow's butter, coconut, and palm-kernel oils.
Undecylic	$C_{10}H_{21}{\cdot}COOH$	186	Undecylin	$C_3H_5(O{\cdot}C_{10}H_{21}CO)_3$	596	20.14	15.44	93.63	
Lauric	$C_{11}H_{23}{\cdot}COOH$	200	Laurin	$C_3H_5(O{\cdot}C_{11}H_{23}CO)_3$	638	18.81	14.42	94.06	Spermaceti, tan oil, coconut, and palm-kernel oils.
Tridecylic	$C_{12}H_{25}{\cdot}COOH$	214	Tridecylin	$C_3H_5(O{\cdot}C_{12}H_{25}CO)_3$	680	17.65	13.53	94.41	
Myristic	$C_{13}H_{27}{\cdot}COOH$	228	Myristin	$C_3H_5(O{\cdot}C_{13}H_{27}CO)_3$	722	16.63	12.75	94.75	Spermacetic, muscat butter, coconut, and palm-kernel oils.
Pentadecatoic	$C_{14}H_{29}{\cdot}COOH$	242	Pentadecatorin	$C_3H_5(O{\cdot}C_{14}H_{29}CO)_3$	764	15.70	12.04	95.03	
Palmitic	$C_{15}H_{31}{\cdot}COOH$	256	Palmitin	$C_3H_5(O{\cdot}C_{15}H_{31}CO)_3$	806	14.89	11.41	95.30	Associated with stearin and olein in most animal and vegetable fats and oils.
Margaric	$C_{16}H_{33}{\cdot}COOH$	270	Margarin	$C_3H_5(O{\cdot}C_{16}H_{33}CO)_3$	848	14.16	10.85	95.52	Seeds of thorn apple, *Datura Stramonium.*
Stearic	$C_{17}H_{35}{\cdot}COOH$	284	Stearin	$C_3H_5(O{\cdot}C_{17}H_{35}CO)_3$	890	13.48	10.34	95.72	See palmitin.
Nondecylic	$C_{18}H_{37}{\cdot}COOH$	298	Nondecylin	$C_3H_5(O{\cdot}C_{18}H_{37}CO)_3$	932	12.87	9.87	95.92	
Arachidic	$C_{19}H_{39}{\cdot}COOH$	312	Arachidin	$C_3H_5(O{\cdot}C_{19}H_{39}CO)_3$	974	12.32	9.44	96.10	Characteristic glyceride of peanut oil.
Medullic	$C_{20}H_{41}{\cdot}COOH$	326	Medullin	$C_3H_5(O{\cdot}C_{20}H_{41}CO)_3$	1,016	11.81	9.06	96.27	Medullic acid is a mixture of palmitic and stearic acids.
Behenic	$C_{21}H_{43}{\cdot}COOH$	340	Behenin	$C_3H_5(O{\cdot}C_{21}H_{43}CO)_3$	1,058	11.34	8.69	96.40	Characteristic glyceride of oil of *ben.*
Carnaübic	$C_{23}H_{47}{\cdot}COOH$	368	Carnaübin	$C_3H_5(O{\cdot}C_{23}H_{47}CO)_3$	1,142	10.51	8.05	96.65	Occurs as an ether in combination with the higher alcohols in carnaübic wax
Hyenic	$C_{24}H_{49}{\cdot}COOH$	382	Hyenin	$C_3H_5(O{\cdot}C_{24}H_{49}CO)_3$	1,184	10.14	7.77	96.79	Free acid occurs in glandular pouches of the striped hyena.
Cerotic	$C_{26}H_{53}{\cdot}COOH$	410	Cerotin	$C_3H_5(O{\cdot}C_{26}H_{53}CO)_3$	1,268	9.46	7.25	96.99	Acid occurs in free state in beeswax and carnaübic waxes.
Melissic	$C_{29}H_{59}{\cdot}COOH$	452	Melissin	$C_3H_5(O{\cdot}C_{29}H_{59}CO)_3$	1,394	8.61	6.60	97.25	Acid occurs in free state in beeswax.

ACIDS OF THE ACRYLIC SERIES—GENERAL FORMULA, $C_nH_{2n-1}COOH$

Acrylic	$C_2H_3{\cdot}COOH$	72		$C_3H_5(O{\cdot}C_2H_3CO)_3$	254				The acid is an oxidation product of acrolein.
Crotonic	$C_3H_5{\cdot}COOH$	86		$C_3H_5(O{\cdot}C_3H_5CO)_3$	296				Acid occurs with isocrotonic acid in crude pyroligneous acid.
Angelic, Tiglic	$C_4H_7{\cdot}COOH$	100		$C_3H_5(O{\cdot}C_4H_7CO)_3$	338	32.54	27.22	88.76	Angelic acid occurs in angelica root. Glyceride occurs in croton oil.
Hypogaric	$C_{15}H_{29}{\cdot}COOH$	254		$C_3H_5(O{\cdot}C_{15}H_{29}CO)_3$	800	15.00	11.49	95.26	Present in peanut oil.
Oleic	$C_{17}H_{33}{\cdot}COOH$	282	Olein	$C_3H_5(O{\cdot}C_{17}H_{33}CO)_3$	884	13.57	10.41	95.70	The characteristic glyceride of all liquid fats.

ACIDS OF THE LINOLIC SERIES—GENERAL FORMULA, $C_nH_{2n-3}COOH$

Elæomargaric	$C_{16}H_{29}{\cdot}COOH$	266	Elæomargarin	$C_3H_5(O{\cdot}C_{16}H_{29}CO)_3$	836	14.35	11.01	95.69	Occurs in Japanese wood oil.
Linolic	$C_{17}H_{31}{\cdot}COOH$	280	Linolein	$C_3H_5(O{\cdot}C_{17}H_{31}CO)_3$	878	13.67	10.48	95.68	Occurs in linseed and other drying oils.

ACIDS OF THE LINOLENIC SERIES—GENERAL FORMULA, $C_nH_{2n-5}COOH$

Linolenic	$C_{17}H_{29}{\cdot}COOH$	278	Linolenin	$C_3H_5(O{\cdot}C_{17}H_{29}CO)_3$	872	13.76	10.55	95.64	Occurs in drying oils, especially linseed oil.

ACIDS OF THE RECINOLEIC SERIES—GENERAL FORMULA, $C_nH_{2n-2}O_3$

Recinoleic	$C_{17}H_{32}OH{\cdot}COOH$	298	Recinolein	$C_3H_5(O{\cdot}C_{17}H_{32}{\cdot}OH{\cdot}CO)_3$	932	12.87	9.87	95.92	Characteristic glyceride of castor oil.

It will be seen from Table X that the amount of alkali required for saturation decreases as the molecular weight of the glycerides increases. Hence, it will be found that those commercial fats and oils in which the glycerides of low molecular weight occur, possess the highest alkali absorption in proportion to their weight.

The greater quantity of salt required for graining the soap made from such stock is due to the presence of those glycerides of low molecular weight whose greater solubility in brine of the sodium salt is a marked characteristic. As the glycerides increase in molecular weight, the solubility in brine of the soap obtained therefrom diminishes; hence, less salt is required for graining.

NOTE.—As shown in *Organic Chemistry*, the homologous character of the simple hydrocarbons of the saturated and unsaturated fatty series extends to all compounds formed from them, either naturally or artificially. The purpose of Table X is to illustrate this property by extending the quantitative characteristics of the more important acids to their corresponding glycerides, and more particularly to those employed in soap manufacture, which appear in heavy type. This table is of great practical interest from the standpoint of both the candle maker and the soap boiler, inasmuch as the most important practical properties of glycerides, namely, alkali absorption and glycerine liberation, are set forth in detail. It will be seen from the standpoint of the soap maker that to the acetic and acrylic series of fatty bodies belong the most important commercial glycerides, namely, stearin, palmitin, and olein, while to the more unsaturated series belong those glycerides characteristic of all drying oils, which are the special consideration of the paint manufacturer.

62. The homologous properties of the glycerides mentioned in the previous article and shown in Table X, are further shown in their practical application in soap making in Table XI, in which is indicated the theoretical yield of anhydrous soap from the glycerides mentioned.

63 The reason for the greater yield of soap from cocoanut oil than from the ordinary animal and vegetable fats is thus made clear Not only is there a greater yield of anhydrous soap in itself, but by virtue of that higher yield a greater degree of hydration and *filling* is thus permissible. In Table XII are given the actual and not the theoretical percentages of caustic potash and caustic soda required in practice to saponify the commercial fats and oils mentioned.

TABLE XI

THEORETICAL YIELD OF ANHYDROUS SOAP

Glyceride and Chief Sources	Molecular Weight	Yield on Saponification With Water		Per Cent. Water Absorbed	Yield on Saponification With Caustic Soda		Per Cent. *NaOH* Absorbed
		Per Cent. Fatty Acids	Per Cent. Glycerine		Per Cent. Soap	Per Cent. Glycerine	
Laurin—coconut and palm-kernel oils	638	94.04	14.42	8.46	104.38	14.42	18.80
Myristin—palm-kernel oils	722	94.74	12.75	7.48	103.87	12.70	16.63
Palmitin—palm oil and tallow	806	95.28	11.41	6.69	103.47	11.41	14.88
Linolein—linseed oil	878	95.68	10.48	6.16	103.19	10.48	13.67
Olein—olive and cottonseed oils . . .	884	95.70	10.40	6.10	103.16	10.40	13.56
Stearin—tallow and lard	890	95.73	10.34	6.07	103.14	10.34	13.48
Recinolein—castor oil	932	95.92	9.88	5.80	103.00	9.88	12.88
Arachidin—peanut oil	974	96.10	9.44	5.54	102.87	9.44	12.31

TABLE XII

PERCENTAGES OF CAUSTIC POTASH AND CAUSTIC SODA TO SAPONIFY COMMERCIAL FATS AND OILS

	Per Cent. *KoH*	Per Cent. *NaOH*
Almond oil	19.5–19.6	13.9–14
Bone fat and grease	19.1–19.7	13.6–14
Butter	22.1–23.2	15.8–16.5
Castor Oil	17.6–18.1	12.5–13
Cod oil	18.5–21.3	13.2–15.1
Cottonseed oil	19.1–19.6	13.6–14
Coconut oil	24.6–26.8	17.5–19.1
Hempseed oil	19.3	13.8
Linseed oil	18.7–19.5	13.3–14
Lard oil	19.2–19.6	13.7–14
Niger seed oil	18.9–19.1	13.5–13.6
Olive oil	19.1–19.6	13.6–14
Peanut oil	19.1–19.6	13.6–14
Palm oil	19.6–20.2	14–14.4
Palm nut oil	22–24.7	15.7–17.7
Porpoise oil	21.6	15.5
Poppy seed oil	19.3–19.5	13.8–14
Rape oil	17.1–17.9	12.2–12.8
Rosin	17–19.3	12.1–14
Seal oil	18.9–19.6	13.5–14
Sesame oil	19–19.4	13.9–14
Sperm oil	12.3–14	8.8–10
Tallow	19.3–19.8	13.7–14.1
Walnut oil	19.6	14
Whale oil	18.8–22.4	13.4–16

BEHAVIOR OF FATS AND OILS TOWARD SAPONIFYING AGENTS

64. The various fats and oils display different characteristics in their behavior toward saponifying agents. Moreover, the chemical reactions of organic compounds do not proceed with the ease and certainty that characterize the reactions of inorganic compounds. In effecting combination between fats or oils and caustic alkalies in a soap kettle, where in many instances the fatty bodies are in excess of 100,000 pounds, the chemical peculiarities of the bodies undergoing change should in every case be thoroughly understood.

65. In a mixture of fats, the individual fats tend to impart their properties to one another. Certain oils, notably coconut and palm kernel, require caustic lye of high density to effect combination. With others, as tallow and palm oil, saponification takes place readily with caustic lye of lower density. Coconut oil requires a caustic lye of at least 20° Baumé, while tallow can be completely saponified with lye no stronger than 18° Baumé. When soap stocks with these characteristics are mixed, the requirements of each are modified so that an oil requiring for saponification alone a lye of high density enters into combination with lye of a density with which it would not combine otherwise without the consumption of a great deal of time and labor. On the other hand, that stock requiring naturally for ready saponification a lye of low density enters readily into combination with a lye of higher density. These peculiarities will be considered in due order.

66. Saponification of Tallow.—Tallow requires a caustic lye of comparatively low density for satisfactory saponification. A 12° Baumé lye, when no subsequent dilution is made, is considered to give the best results. On boiling with open steam, a lye of 18° to 20° Baumé is the highest density practicable. When open steam is used with caustic lye of this density, tallow is the most easily saponified of all glyceride soap stocks, and the soap formed is most easily grained.

Sodium stearate, which constitutes the bulk of the anhydrous soap made from tallow, is one of the least soluble in water of all the alkaline salts of the fatty acids, as it undergoes practically no change when treated with 10 parts of water; neither is its hardness appreciably affected. This quality manifests itself in the inferior lathering properties of pure tallow soap.

For this reason other oils are used. In making a laundry soap, rosin is added for the same purpose. Furthermore,

TABLE XIII

POUNDS OF TALLOW SAPONIFIED BY 100 POUNDS OF CAUSTIC SODA OF DIFFERENT DENSITIES MADE FROM VARIOUS GRADES OF CAUSTIC

Density, Degrees Baumé	Grade of Caustic Soda					
	77½ Per Cent. *Na2O*	76 Per Cent. *Na2O*	74 Per Cent. *Na2O*	72 Per Cent. *Na2O*	70 Per Cent. *Na2O*	60 Per Cent. *Na2O*
	Tallow Saponified Pounds	Tallow Saponified Pounds	Tallow Saponified Pounds	Tallow Saponified Pounds	Tallow Saponified Pounds	Tallow Saponified Pounds
10	46.78	45.86	44.66	43.45	42.24	36.20
12	57.14	56.03	54.55	53.08	51.59	48.49
15	71.85	70.46	68.60	66.74	64.88	60.96
18	90.02	88.26	85.94	83.62	81.28	69.66
20	102.64	100.60	97.95	95.30	92.64	79.39
22	113.64	111.40	108.50	105.50	102.60	87.92
25	132.71	130.10	126.70	123.30	119.90	102.70
28	153.00	150.10	146.10	142.10	138.10	118.40
30	169.07	165.80	161.40	157.00	152.60	130.80
35	205.92	201.90	196.60	191.30	186.00	159.30

on aging, a pure tallow soap becomes so hard as to give very little lather, so that its use is not economical for either household or laundry purposes. The comparative insolubility in water of sodium stearate is also shown in the readiness with which tallow soap dries. Its presence in admixture with other fats imparts firmness, or body, to the soap, thus enabling a greater proportion of softer stock, or that fatty acid whose sodium salt has a greater affinity for water, to be incorporated.

The use of sodium stearate thus increases the amount of water that may be incorporated with a soap without an excessive sacrifice of firmness. It is the best raw material for the manufacture of grained soaps and admits of the greatest yield of all the animal soap stocks. With its use, the various chemical and physical changes occurring in the soap kettle during the process of boiling are well defined and of easy recognition.

67. In Table XIII is expressed the saponifying power of caustic lyes of different densities made from chemically pure and ordinary grades of caustic occurring in the market. By this table, the amount of stock that can be saponified by any quantity of lye of the density and quality given may be readily determined within limits of accuracy suitable for all technical purposes to which the table may be applicable.

68. Saponification of Cottonseed Oil.—Refined cottonseed oil saponifies with difficulty and only after continued boiling, especially when saponified alone. The absence of free fatty acids tends to retard saponification. Combination with alkali is hastened when tallow is present, or upon the addition of soap scraps. Saponification is best begun with a 15° Baumé lye.

Pure cottonseed-oil soap is white, with a firmness determined largely by its degree of hydration. It consists almost entirely of sodium oleate. This compound is soluble in 10 parts of water, while sodium stearate, as already shown, is not appreciably affected by this volume. In accordance with its greater solubility in water, sodium oleate has in comparison greater and peculiar lathering properties. It lathers more readily than does sodium stearate, but instead of the firm lather of tallow soap, obtained only after much rubbing, it gives a shiny, thin lather peculiar to all soaps made of stock consisting largely of olein, for example, Castile soap and cottonseed-oil soap stock. Cottonseed oil is generally used in admixture with varying proportions of tallow and grease.

A good settled soap of cottonseed oil alone is not practicable. Soap thus made is *thin* and lacks the body and durability of

a tallow soap or a soap made from mixed stock. By the use, however, of a large proportion of soda ash and sodium silicate, an artificial firmness may be imparted.

Cottonseed-oil soaps *sweat* readily, and unless the oil has been refined with care, they discolor rapidly and become rancid. The brownish or yellowish blotches seen in soaps containing cottonseed oil may be traced to the imperfect removal of the coloring matter of the seed during the refining process.

69. Saponification of Coconut and Palm-Kernel Oils.—Coconut and palm-kernel oils differ from all fatty bodies employed in soap manufacture in the greater quantity of alkali required for saponification, in the greater quantity of salt required for graining, and in the greater yield of soap produced, the quality of which permits the greatest amount of hydration and filling. The difficulty of graining these soaps with dry salt or brine is overcome by using strong caustic lye for graining.

Pure coconut-oil soap is white, brittle, and hard. The oil is a valuable addition to cottonseed oil and tallow, and it yields a soap possessing qualities superior to that possessed by either stock alone. It enters into combination with alkali with extreme ease, which property especially adapts it for soap manufacture by the cold process.

During saponification considerable heat is evolved, and when once begun, saponification takes place with such rapidity that the contents of the kettle, unless carefully watched, will boil over. On the stock change (stock saponification), difficulty is often experience in working with coconut oil, or a mixture of oils containing coconut oil, the soap mass becoming thick easily. This is due to the high absorption of water consequent to rapid saponification and may be overcome by retarding the rate of combination of caustic alkali and oil. This is best effected by adding brine when the soap mass shows signs of becoming thick. It may also be provided by adding the oil slowly to the caustic alkali already in the kettle, at the same time boiling vigorously.

70. Coconut oil combines with weak and strong caustic lyes with equal facility, but in practice in the boiling of settled soap, a density of from 20° to 25° Baumé is commonly used. Coconut-oil soap when hot is very fluid, smooth, and transparent; when cold, it becomes so hard as to be cut only with difficulty. It dissolves readily in water, yielding a quickly formed, profuse, but not permanent, lather. It is caustic to the tongue even though no free alkali is present, and when used for toilet purposes in excess of actual requirements, it irritates and reddens the skin. If coconut oil is not completely saponified, the soap made from it soon becomes rancid and odorous. It dissolves freely in salt water and is the fatty basis of the so-called marine, or salt-water, soaps.

71. The complex composition of coconut oil suffices to explain the peculiarities of its behavior toward saponifying agents and the properties of the soap made from it. Coconut and palm-kernel oils contain a greater variety and quantity of glycerides of fatty acids of low molecular weight than any other soap stock.

As will be seen by referring to Table XI, these bodies possess a higher alkali absorption, yield a greater percentage of glycerine on saponification, are more soluble in water when free and combined with alkali, and, in general, possess less stable chemical properties than do similar bodies of higher molecular weight that occur commercially as soap stock.

72. Saponification of Palm Oil.—Palm oil, of which palmitin is the chief glyceride, finds only limited use as a soap stock in the United States. This oil is used chiefly as an ingredient of certain toilet-soap bases (for which purpose it is well adapted by its perfume) and to disguise the odor of rosin in soap of a high rosin content. In Great Britain and continental Europe, however, it replaces tallow to a large degree.

Sodium palmitate so closely resembles sodium stearate in its chemical properties that the statements concerning the properties of the latter salt are directly applicable to it. Palm oil saponifies very readily, owing to the high percentage of free fatty acids characteristic of the oil.

73. Saponification of Rosin, or Colophony.—Rosin when in a pure state consists of the anhydrides of the rosinic acids, chiefly abietic acid, $C_{18}H_{27}(CO_2H)$. On boiling, rosin is readily transformed into the acid, which combines with both carbonated and free alkali. Rosin may be *killed*, or saponified, alone or added after the kettle has been charged with tallow. The tallow may be saponified previously or both stocks may be killed together. The difficulty with which a pure rosin soap separates, or grains, in even a concentrated salt solution is the chief reason for its not being saponified alone. This is due to the fact that the specific gravity of rosin ranges from 1.07 to 1.10, while that of tallow is about .9. Soda ash may be used as the saponifying agent. The rosin soap thus made is frothy from the liberation of carbonic-acid gas, and as a result of the increased volume caused in this manner, much kettle space is required to work it. This saponification may be carried out by using a separate kettle and saponifying one or more charges at one time, pumping out the amount needed for each charge. However, where factory conditions are such as to warrant the use of soda ash instead of caustic soda, a considerable saving is possible, as is shown in the following approximate calculation:

EXAMPLE.—6,000 pounds rosin $\times .13 = 780$ pounds, approximately, of 74-per-cent. (see Table XII) caustic soda required for combination; $\frac{74}{60} \times \$1.75 = \$2.16$, cost per 100 pounds of 74-per-cent. caustic soda when price is \$1.75 per 100 pounds for 60 per cent.; $\$2.16 \times 7.8$ hundredweight $= \$16.85$, cost of 74-per-cent. caustic soda, required for combination.

$$2NaOH : Na_2CO_3 = 780 : x$$
$$80 : 106 = 780 : x$$

or

$x = 1{,}033.5$ pounds soda ash required for combination.

$1{,}033.5 \times \$.0009 = \$9.30$, cost of soda ash required for combination.

Caustic soda costs	\$16.85
Soda ash costs	9.30
Saving in alkali for 6,000 pounds of rosin	\$ 7.55

74. The alkali salts of the rosin acids are very hygroscopic and naturally readily soluble in water, and, as should be expected, make a very soft soap. They detract from the firmness of all soaps in which they enter. Rosin betrays its presence in the finished soap by the darker color and by its

characteristic odor and stickiness, which latter property is due to the marked affinity of the alkaline resinates for moisture.

This peculiarity manifests itself in the readiness with which poorly made rosin soaps sweat. The marked detergent property, ready solubility in either hot or cold, soft or permanently hard water, and cheapness of the alkaline resinates, make them an indispensable addition to the firmer tallow soap for domestic purposes. The characteristic odor may be ameliorated by the addition of suitable perfumes, and the stickiness may be reduced by the admixture in reasonable proportions of the tallow and rosin base. Highly rosined soaps become very dark on aging.

With rosin of the M and N grades of not more than 50 per cent. of the weight of stock, good laundry soaps of light color and excellent texture can be made by the method described later. These soaps are also free from sweating and rarely ever show any crystallization of salts on the surface.

75. The best proportions of tallow and rosin to employ depend primarily on the firmness of the tallow; that is, on the percentage of stearin present. This proportion also changes with the season, less being used in summer than in winter. A soft tallow cannot assimilate so much rosin as a firm tallow and the desired firmness of the finished soap be obtained.

It has been the custom of the trade to rate rosined soaps according to the proportion that the rosin bears to the fat stock by what is known as soapmakers' percentage. A 100-per-cent. rosin soap contains equal parts of tallow and rosin; a 50-per-cent. rosin soap contains 2 parts tallow and 1 part rosin; a 150-per-cent. rosin soap contains 1 part tallow and 1.5 parts rosin.

A soap properly made of these ingredients and in the proportion of 100 pounds of tallow and 50 pounds of rosin, with not more than 6 per cent. of soda-ash solution added in the crutcher, constitutes the standard high-grade settled rosin soap.

76. Saponification of Olive, Red, Corn, and Cottonseed Oils.—Olive, red, corn, and cottonseed oils possess

the same general chemical characteristics and behave in the same manner toward saponifying agents.

Olive oil was originally the basis of the soap known to Americans as Castile soap and on the continent of Europe as Marseilles soap. Pure olive-oil soap is white and very mild in its detersive action. It is composed chiefly, if caustic

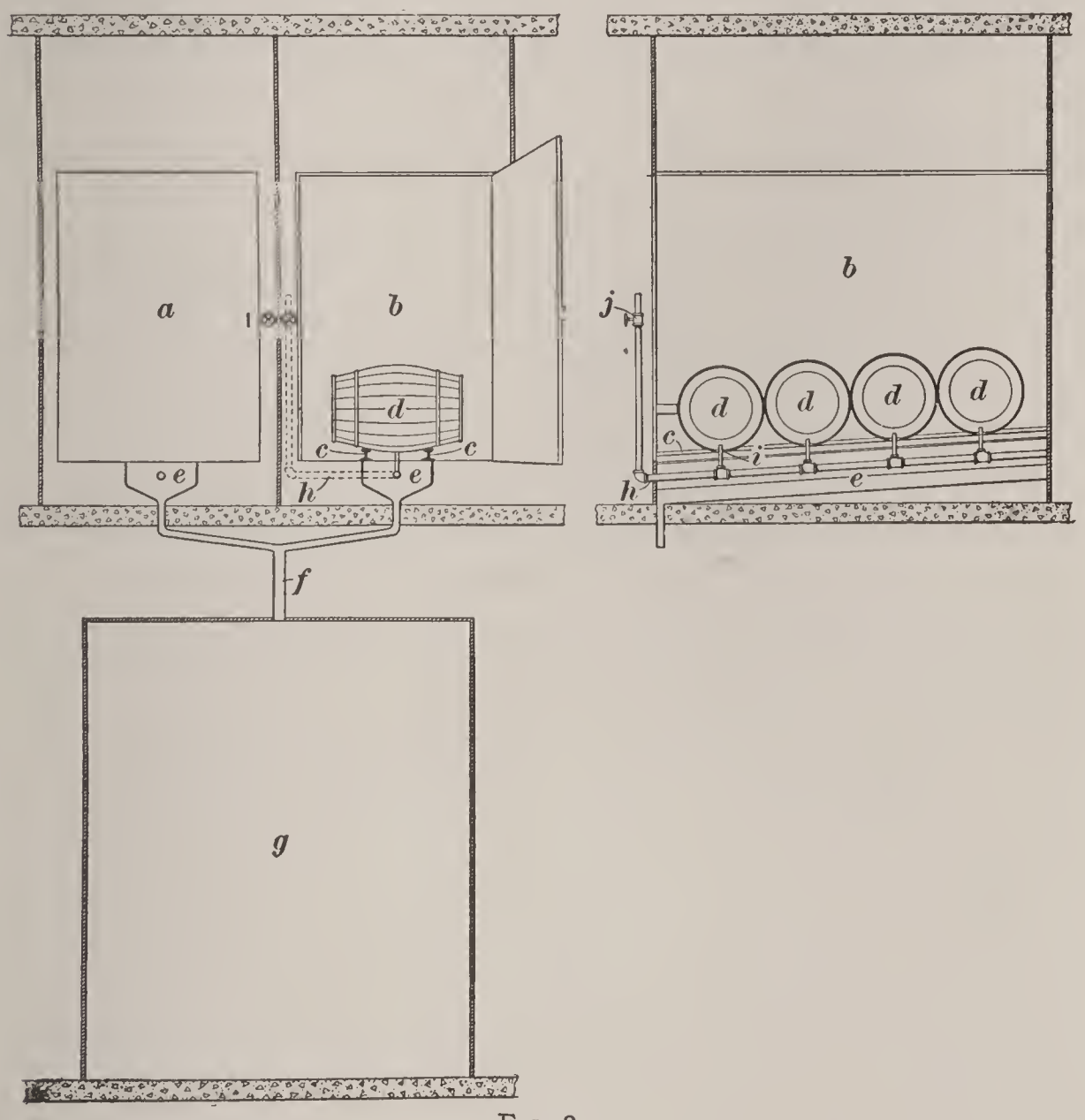

FIG. 8

soda is used to effect saponification, of sodium oleate. It is an excellent ingredient of a toilet-soap base and is especially adapted for use in the textile industry.

Red oil, or commercial oleic acid, being a stronger acid than carbon dioxide, can be saponified to the extent of about 90 per cent. with soda ash. Red-oil soap, sometimes called oleine soap, is practically identical in its composition and

properties with olive-oil soap, and is therefore equally adapted for the cleansing of textiles.

Cottonseed-oil soap stock, when in a clean condition and as free as possible from coloring matter, is identical in composition with red-oil soap and is adapted for the same technical uses. In connection with the use of cottonseed-oil soap stock, it should be remembered that it is simply soap, and unless in a very dehydrated condition does not admit of the yield common to all glyceride stock. It is simply an addition used because of its cheapness.

77. Removal of Stock from Containers.—The stock is received in barrels, tierces, drums, hogsheads, pipes, or puncheons. In some cases, factories are located so that it can be handled in tank cars. A typical melting room, two views of which are shown by Fig. 8, is generally located on the first floor and directly over tanks which receive the melted stock. It is usually a room with the sides and floor sheathed with iron plates and provided with two or more compartments *a* and *b* so that one charge may be melting while another is being set.

There is a track of inclined rails *c* in the center of each compartment on which the containers *d* easily roll. The gutter or pan *e* is placed directly beneath the container, and is also inclined in order that the melted stock will run forward and discharge to the pipe *f* which connects it with the stock tank *g*.

The inlet of this pipe has a strainer to keep out the bungs and foreign material that would block the pipes and pump. The steam line *h* with valves and swing nipples *i* is laid in the center of the track at intervals to accommodate the different size containers. The steam-control valve *j* is located outside the compartment.

When the charge has been set, blocked, and nipple adjusted to the bung of the container, the steam is turned on. In the case of fluid oils, it is not necessary to use any steam until all the fluid material has run out and then only for a short time. The length of time depends on the season. As the containers are removed they are examined with a light to make sure that they are empty.

78. Storage Tanks.—The best arrangement of storage tanks is to have a sufficient number to take care of not only the different kinds of stock but of the different classes of each stored. This calls for an assortment of both large and small tanks. These tanks are provided with closed steam coils so as to keep the stock melted and in shape for pumping and gauges on the sides graduated usually in 1,000-lb. units.

The stock received in the melting-out tank is allowed to settle. It is very necessary to store fats and oils as dry as possible to prevent decomposition. The melting-out tank is then emptied to the storage tank by a pump. The pump is fitted with a pet-cock by which samples can be drawn when the indicator on the tank shows the level at which water may be expected. As soon as water appears, the pump is shut off. This water is pumped to the first kettle taking a stock charge.

It is good practice to connect all the drips from the storage-tank coils into a small tank and examine this tank for indications of leaky coils. The tanks themselves will indicate leaky coils when they show more content on the gauge than the inventory carried on the tank. Once a week all the tanks should be tested for water and the stock kept dry.

79. Piping.—One of the most important features about all piping in a soap factory is that all lines from tanks or kettles to pumps be equipped with *steaming-out* lines. The piping is so arranged with stop valves that live steam can be turned into them and the entire line of communication made clear before any transfer of material is attempted. It is also just as vital that as soon as any pump has delivered its final charge that the entire line be again steamed out both ways, that is from pump to kettle and from pump to tank before the valves are closed.

It is not a rare thing to come into a soap factory on a morning in winter and find lines blocked because of the failure to have the lines steamed out. This steaming-out applies to all lines carrying soap or lyes.

MANUFACTURE OF SOAP

Serial 2055B (PART 2) Edition 1

PROCESSES OF SOAP MANUFACTURE

GENERAL REMARKS

1. The process of soap boiling consists essentially of effecting a chemical reaction between a fatty body and a caustic alkali or between a fatty or resinous acid and a carbonated alkali. The manner of bringing about this combination and the conditions under which the reaction is completed give rise to three general classes of soap-manufacturing processes, namely, boiled, semiboiled, and cold processes, whereby soaps, to which the same descriptive terms may be applied as well, are produced.

Boiled soaps are also called *settled soaps* when in process of manufacture they have been subjected to changes by means of which the soap is purified and the glycerine separated.

A *semiboiled soap* is one that has not been subjected to a graining process, but contains all the material added to the kettle. It is also called a *run soap,* which term, however, is without technical significance.

A *cold soap* is one made by the direct combination of the materials in the proportions in which they are to remain in the finished soap, the combination being effected without the aid of heat other than that required to bring the ingredients to the requisite temperature and that evolved by the chemical reaction.

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The classification of processes just given is arbitrary and is not based on any essential chemical differences in the processes. The division is more mechanical than chemical and has reference chiefly to the time required, the artificial heat employed, and the mechanical apparatus necessary to a satisfactory operation of the process.

The production of a good boil of soap is dependent entirely on the judgment used by the soap boiler. His operations are due to the knowledge that experience has taught him. The successful boilers are keen observers, and, outside of one chemical test for free alkalinity, they depend solely on the looks of the kettle as it is boiling. Some boilers become so expert that they can estimate quite closely the free alkalinity of stock changes by the taste.

MANUFACTURE OF BOILED OR SETTLED SOAPS

BOILING-ROOM PROCESSES

2. Boiled Soaps.—The boiled soaps are the most important and constitute the class most generally manufactured and used. All laundry soaps, as well as the base for toilet soaps, are made by this process.

Before discussing in detail the manufacture of soap of this class, the essential features of the process as it is continued throughout the time required for its completion will be considered. There is arranged in Table I what may be called the outline of a boil of settled rosin soap. In this table is embodied an outline of the most important details of a boil of soap of this character. It is the soap most commonly made in the United States, and the procedure here outlined is the one generally followed.

In an elaboration of the treatment given the soap in the kettle will be discussed the directions and precautions to be observed, from the addition of the soap stock and alkali to the kettle, through the various changes to the transferring

TABLE I

OUTLINE OF A BOIL OF SETTLED ROSIN SOAP

Change	Material Added to Kettle	Saponification Agent	Graining	Disposition of Lye
First or stock....	Tallow, oil, grease.	18° Bé. caustic-soda lye.	Salt or brine	Drawn to empty tank and then to storage tanks for glycerine recovery.
Second, third, etc., wash changes...		18° Bé. caustic-soda lye to hold a free alkalinity of at least 20 per cent.	Salt or brine	Drawn to empty tank and then run to sewer.
First rosin.....	Rosin either in lumps or previously saponified scrap soap. Second rosin lye.	25° Bé. caustic-soda lye to hold a free alkalinity of 2 to 3 per cent.	Caustic-soda lye	Pumped to any first rosin change.
Second rosin.....	Boiled-up niger of previous boil.	25° Bé. caustic-soda lye to hold a free alkalinity of 3 to 4 per cent.	Caustic-soda lye	Pumped to any second rosin change.
Strong	Strong change lye.	Water or 3°–4° Bé. caustic-soda lye.	None	
Finish or settle water				None.
Niger				Boiled and pumped to any second rosin change.

of the product to the crutcher and the addition of filling agents, to its final treatment in the drying room and its preparation for shipment.

3. The following soap-boiling process is carried out in factories where the maximum yield of glycerine is striven for. A yield of glycerine from 8 to 8½ per cent. is possible by following this method, when high-grade stock is used.

First change: Into a kettle from which the niger of a previous boil has been pumped on a second rosin change, run in water enough to cover 6 inches of the kettle bottom and boil with open steam. The stock pump is started and 18° Bé. caustic-soda lye is added simultaneously. Where grease, tallow, and oil are used, they are usually saponified in that order. When the saponification has started, noted by the swelling of the mass, the steam is eased off; only enough is used to keep the contents well mixed. This also serves to save room for the subsequent boiling. This change is complete when two boilings and tests show a free alkalinity of .20 per cent. Dry salt or brine is added until the soap becomes very *open* and the lye drops out clear.

Second change: Every effort is made to remove all the possible glycerine before adding rosin because in the best practice no rosin lyes are sent to the glycerine plant. Therefore, a number of these wash changes are made.

After the first lye has been drawn and sent to the glycerine-lye storage tanks, water and a small amount of 18° Bé. caustic-soda lye are added to the kettle and the whole mass brought to a good vigorous boil with open steam. Water enough is used to *close* or *flatten out* the soap and enough caustic lye to hold the alkalinity up to .20 per cent. It is grained with salt like the first change and the lye drawn and disposed of as before.

Third, fourth, and fifth changes: The number of these wash changes is dependent on the practice and experience of the individual plants. They depend also on the amount of water used on each change, the price of glycerine, the amount of exhaust steam available, the amount of glycerine-lye stor-

age, and the capacity of the evaporators. The water used is usually expressed in terms of the stock and varies from 250 to 450 per cent. A stock charge of 10,000 pounds will make a glycerine lye of 25,000 to 45,000 pounds. The procedure for these changes is the same as for the second change.

First rosin change: When the last wash change has been drawn, scrap soap, a small amount of recovered salt (usually high in sulphate), and enough 25 to 30° Bé. caustic-soda lye to *open* or grain the soap, is added. The alkalinity is kept up to 2 to 3 per cent. A second rosin lye is pumped in while the rosin is being added and the kettle kept at a good boil. This change is grained on the caustic lye, and, after settling, the waste lye is drawn to an empty kettle and run to the sewer.

Second rosin change: After the first rosin lye has been drawn off, enough caustic-soda lye of 25 to 30° Bé. is added to bring the alkalinity up to 3 or 4 per cent. A boiled-up niger is pumped in and the contents of the kettle vigorously boiled.

Strong change: When the second rosin lye has been drawn, open steam is turned on and enough water or 4–5° caustic-soda lye is added to flatten out the soap. When the mass is homogeneous and entirely flattened out, the steam is shut off and the kettle allowed to settle.

Finish or settle: As soon as the strong change lye has been pumped off, the soap is boiled up and usually small amounts of water worked in with slow boiling. This is continued until the soap boiler is satisfied that the soap has all the characteristics needed. The steam is then shut off and the soap allowed to stand until ready to frame.

4. Soap Kettle.—The soap kettle is made of steel plates of a thickness determined by its capacity. The plates are very carefully riveted and then calked to make them tight. Kettles are either square or rectangular; or cylindrical or slightly truncated. The first type is about 6 inches deeper in front than in back so as to provide a good pitch for draining, while the second type pitches to the center. Kettles of square or rectangular cross-section are more economical of space and make for a cleaner kettle room. It is necessary to brace the

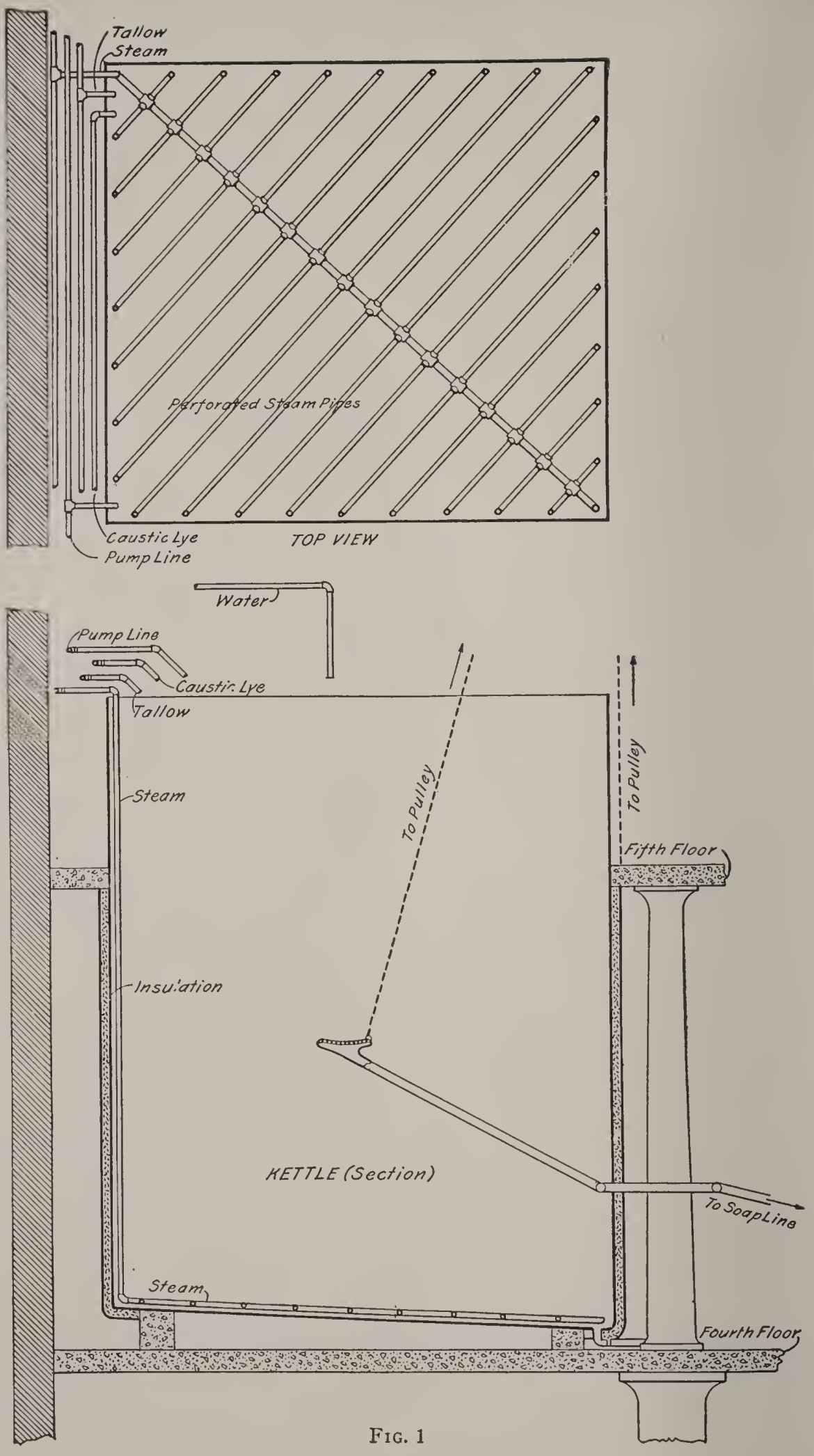

Tallow
Steam
Perforated Steam Pipes
Caustic Lye
Pump Line
TOP VIEW
Water
Pump Line
Caustic Lye
Tallow
Steam
Insulation
To Pulley
To Pulley
Fifth Floor
KETTLE (Section)
To Soap Line
Steam
Fourth Floor

FIG. 1

square and rectangular types with cross-rods, while the cylindrical types do not need them. For the manufacture of laundry soap alone, only open steam coils are provided. These coils are laid along the bottom. The steam header is extended down one corner of the kettle and the main arm is laid across to the other corner just off the bottom of the kettle, as shown in Fig. 1. This main arm has projecting arms of varying length which present a large heating surface. The arms have small holes drilled into them.

5. The steam-control valve is in the main line at the top of the kettle, and between it and the soap line a small vent pipe with a valve is fitted. At about the usual niger level, an opening into the soap line is provided and on the inside of the kettle this opening is fitted with a swing joint and pipe that can be lowered as the soap is being withdrawn.

On the boiling floor, the piping of each kettle is arranged for stock from the storage tanks, caustic-soda lye from the strong lye tank, steam, water and, a line by which lyes from any one kettle may be pumped into any other kettle. Connected to this line and also to the lowest part of the kettle there is a second line for drawing off the glycerine and rosin lyes. This line is also used for pumping nigers, strong change and second rosin lyes.

6. During the boiling, but especially for the settling, it is important as well as economical to conserve all the heat. Therefore, all the kettles are heavily insulated on the sides up to the boiling-floor level. Usually this insulation consists of 3 inches of magnesia-asbestos blocks wired on and covered with $\frac{1}{2}$ inch of asbestos cement. This is covered with canvas and painted.

A very good layout of kettles is one that provides for an empty kettle at all times, that is, one in which no soap is made. In large plants there is one of these kettles for every ten. Into this kettle all glycerine and rosin lyes are drawn, and by watching from the top, the valves on the soap kettle being emptied can be closed at the first sign of soap appearing in the kettle into which the glycerine lye is being run. The lye can

then be sent to glycerine-lye storage tanks or in the case of rosin lyes direct to the sewer. If any soap has run in with the lye, it can be skimmed off and returned to the soap kettle. Fig. 2 shows the kettle-room arrangement, kettles, and piping plans.

7. The arrangement of the steam piping in a round soap kettle is a very important matter, as the successful handling of the contents of the kettle depends a great deal on the shape, diameter, and distribution of the coil. The diameter of the kettle will determine whether one or two open steam coils should be used. With a small kettle, one open steam coil or a crisscross jet in the center will suffice. This crisscross jet is shown at *f*, Fig. 3. With a kettle from 15 to 20 feet in diameter, a second open steam coil around the sides is necessary. The closed steam coil should completely cover the bottom of the kettle. Such a coil, with an open steam coil in the center, is shown in Fig. 4, in which *a* represents the central open steam coil, and *b* and *c*, respectively, the inlet and the outlet of the closed steam coil.

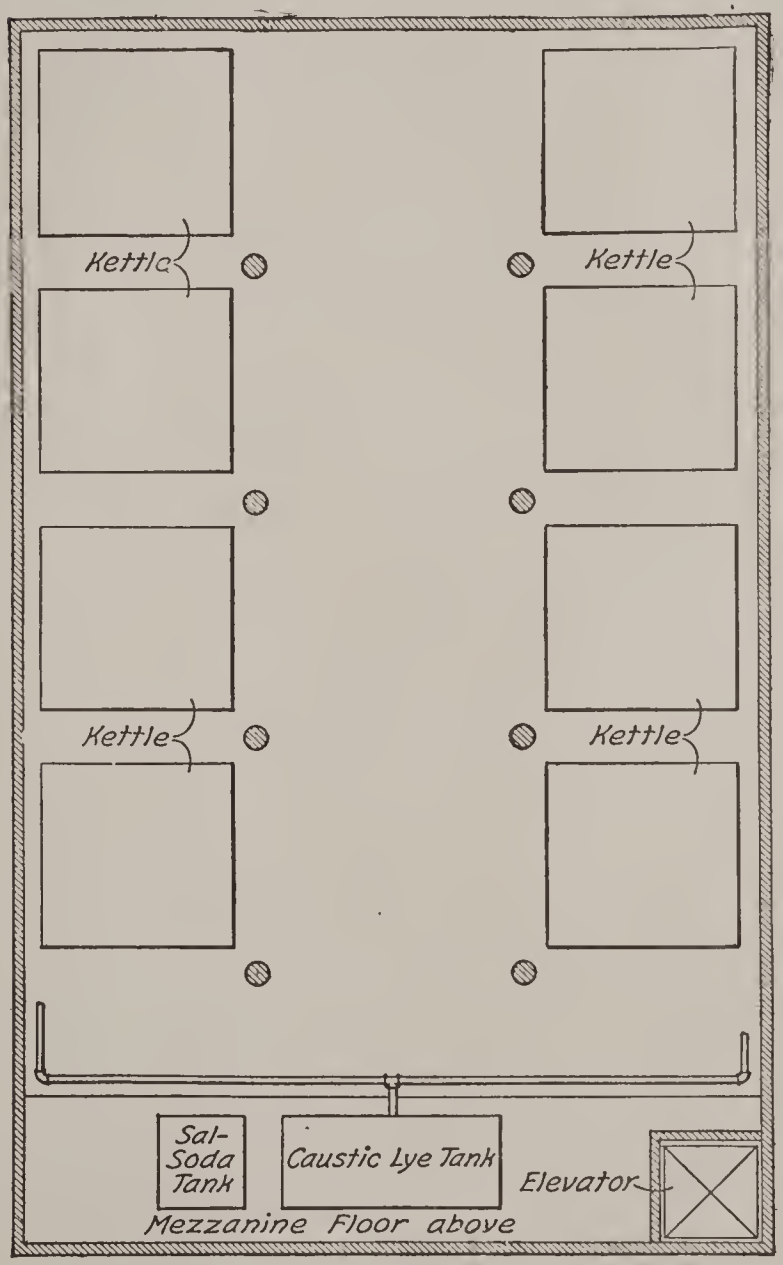


FIG. 2

8. The single pipe coil for closed steam, shown in Fig. 4, is more expensive than the jointed coil shown in Fig. 3, but

is not so liable to leak. The jointed steam coil is cheaper, more quickly and easily installed, and may be enlarged or repaired with only little trouble and expense. The only disadvantage is the greater possibility of leakage, because of the numerous threaded joints. The valves on both the open and closed steam coils should be within easy reach of the soap boiler, in order that the boiling process will be under control at all times.

9. The amount of stock that can be *killed* in a kettle of given capacity varies with the method of working. In general

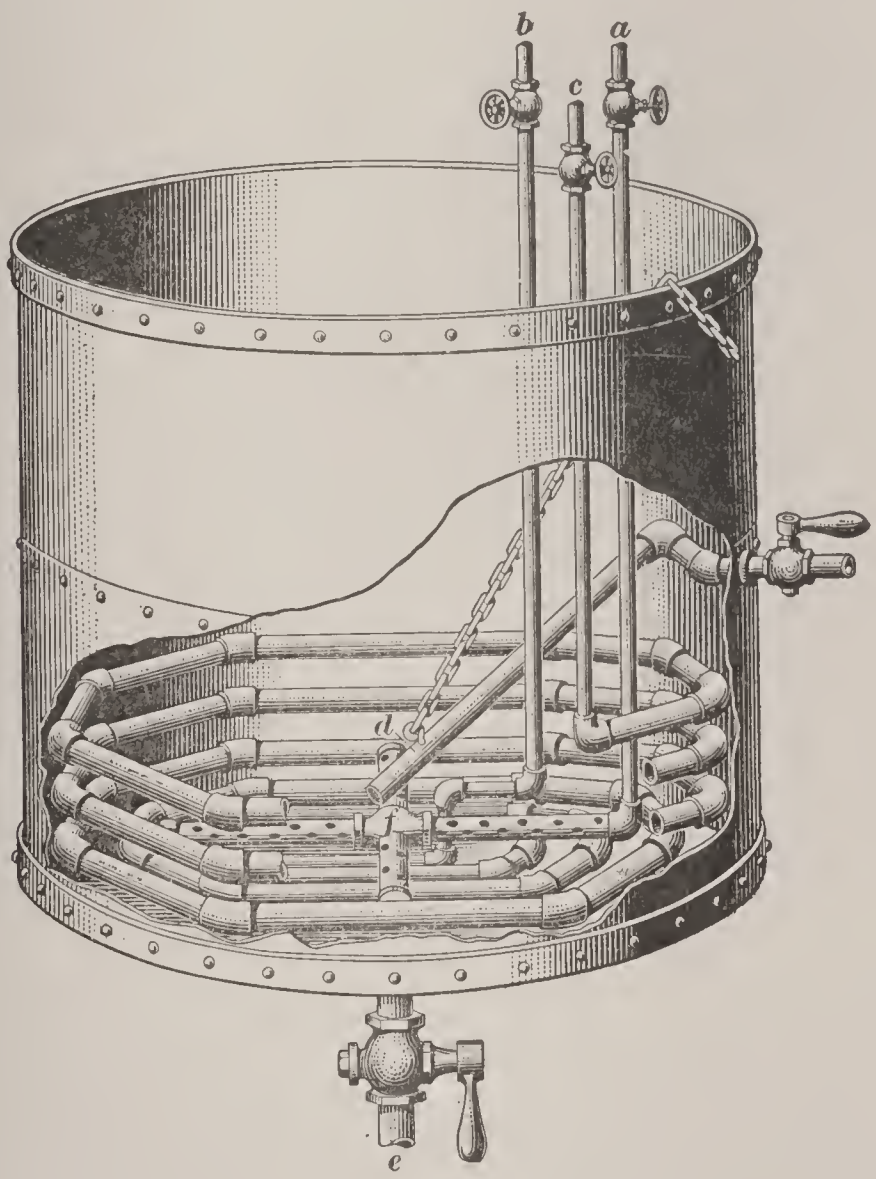


FIG. 3

terms, it may be stated that 1 cubic foot of space is allowed for every 12 pounds of stock to be saponified, or for every 100 pounds of stock.

10. Saponification or Stock Change.—In this discussion the following combination of stock and rosin will be used:

Stock and Rosin Ingredients	Pounds	Percentage
Tallow	28,000	90
Cottonseed oil or grease	3,000	10
		Percentage on Stock
Rosin, 36 bbl.	15,500	50

This combination will produce an excellent laundry soap. However, the proportions and ingredients may be modified, depending on the quality of soap desired. The kettle used is 12 feet 6 inches long, 13 feet wide, 16 feet deep at the rear end, and 16 feet 6 inches deep at the front end.

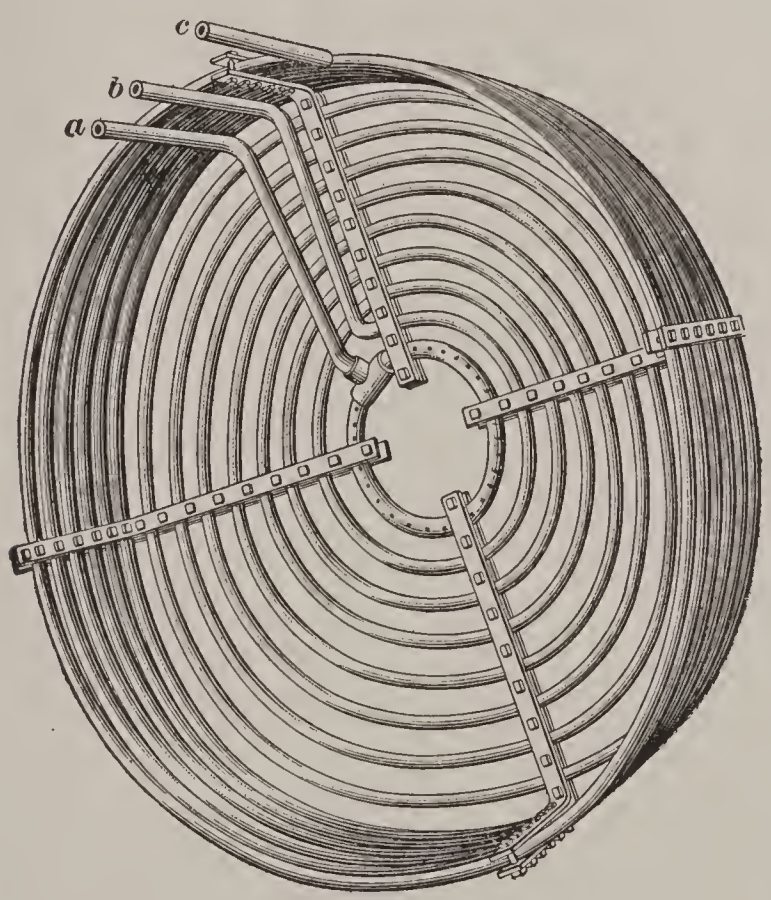


Fig. 4

11. With the variation prevailing in the quality of the raw materials, both organic and inorganic, used in the manufacture of soap, calculations cannot be made with accuracy. The amount of alkali theoretically absorbed by a given stock can be ascertained, however, and the quantity thus calculated can be used, but not infrequently will it be found that the soap will contain either a greater or smaller quantity of free alkali or more or less unsaponified matter, and unless a person has practical experience in soap boiling, it is almost certain that the soap will contain both.

Experience gained by working over the soap kettle is the final arbiter. The conscientious man will use the calculations

of theory and supplement them with his practical knowledge. It is better to have a small quantity of unkilled stock on the stock change and the alkali completely absorbed than to have an excess of alkali wasted in the stock lye.

12. Stages of Saponification.—The saponification of glyceride stock requires three stages for the complete formation of glycerine and the combination of the alkali with the fatty acids. While these stages do not admit of exact definition in the soap kettle, they manifest themselves in certain characteristic conditions, which are familiar to every soap boiler, namely, the emulsion formed on admixture of stock and lye, the pasty mass obtained on continued boiling, and, lastly, the final condition resulting from boiling the pasty mass with an amount of alkali sufficient for complete saponification. By means of chemical formulas, the three successive stages of saponification may be represented graphically:

Raw Materials:

Stearin (tallow), $C_3H_5(C_{18}H_{35}O_2)_3$ Caustic soda: $3NaOH$

1. Emulsion, $C_3H_5OH(C_{18}H_{35}O_2)_2$ Soap: $3C_{18}H_{35}O\cdot NaO$
   Soap: $C_{18}H_{35}O\cdot NaO$
2. Pasty mass, $C_3H_5(OH)_2(C_{18}H_{35}O_2)$ Caustic Soda: $2NaOH$
   Soap: $2C_{18}H_{35}O\cdot NaO$
3. Glycerine, $C_3H_5(OH)_3$ Caustic Soda: $NaOH$

The chief care is to add the stock and alkali simultaneously, with vigorous boiling, and in such proportions that, after saponification has started, the mass can be kept well open until the greater part of the alkali has been added.

13. While the alkali and stock are being run in together, the mass in the kettle must be kept homogeneous by vigorous agitation or by boiling with live steam. Unless maintained in agitation, too little alkali is liable to cause *bunching,* by which is meant local saponification enclosing a mass of unkilled stock. Vigorous boiling will disintegrate and distribute this mass. An excess of alkali grains the mass, thus throwing it, as it were, out of solution, whereby combination is retarded. By the time the total amount of stock has been

added, the greater part of the alkali should also be in the kettle, and boiling is continued, though less vigorously than at the beginning.

14. Care should be taken to avoid an excess of alkali, and at the end of the change it should be added in small quantities only and not until the strength of the quantity previously added has been absorbed. When the stock has been completely killed, the soap should slide freely from a paddle in large, transparent flakes. A small portion rubbed between the fingers should curl up smooth and dry and without any indication of grease. At this stage the contents of the kettle should boil smoothly, rising in the middle and descending at the sides, the appearance being very characteristic.

On the completion of saponification, the contents of the kettle has become a clear, homogeneous mass, in which is present everything that was added during this stage, namely, soap, glycerine, water, and some sodium chloride, sodium sulphate, and sodium carbonate, which were introduced as impurities with the caustic-soda lye. In addition, the mass contains more or less mucilaginous or albuminous matter that was present as animal tissue in the stock.

15. Testing for Free Alkalinity.—The free alkalinity of soap lyes is of the greatest importance. Every effort must be made to *kill,* or saponify, all the stock on the first change. It is just as important that the glycerine lyes be drawn as low in alkalinity as possible, because the more alkali they contain the more treatment they need before the evaporation can be started. A test for free alkalinity has been devised so simple that any man around the kettles can be taught its use in a short time.

When the soap boiler is satisfied that the condition of the kettle warrants a test, a sample of soap is taken out with a long-handled can, while the soap is boiling toward the top of the kettle. Parts of this sample may come from different areas of the kettle, but the locality near the caustic-lye inlet must be avoided as there is generally a small drip there. The can used has a small hole punched in its side near the bottom.

Dry salt enough to bring the sample to a good grain is stirred in. The can is kept tilted away from the hole. When it has stood long enough to drop a clear lye, the lye is drawn into a clean sample bottle by tilting in the opposite direction. The steam on the kettle is shut off while the test is being made.

16. The cylinder used has special etchings on the side so that at the usual 10 c. c. mark, the word LYE is placed beside the mark. At a mark 20 c. c. farther up the word WATER is placed in a like manner. A mark is put for each 2 c. c. and the half and full per cents. are etched on the sides. For all purposes a cylinder showing 4 per cent. alkalinity, will answer. The usual form of cylinder used is shown in Fig. 5.

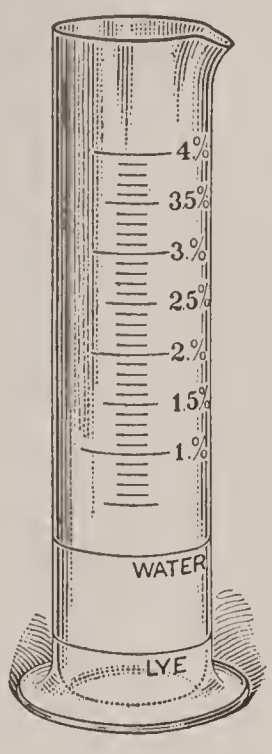


FIG. 5

The test solution $\frac{N}{8}$ sulphuric acid is made and standardized in the laboratory. A bottle of distilled water and an alcoholic solution of phenolphthalein is provided. The acid and distilled-water bottles have quick-filling uncalibrated burettes for easy manipulation.

The test is made by adding the sample of lye in the clean cylinder to the lye mark, a few drops of phenolphthalein and water to the water mark, and shaking to mix well. The $\frac{N}{8}$ sulphuric acid is then added until the color is discharged.

The percentage of free alkalinity is then read directly on the cylinder. Each 2 c. c. of $\frac{N}{8}$ acid used equals .10 per cent. of free alkalinity.

The steam is turned on and when the soap has boiled through completely for a few minutes, the test is repeated. If it holds the same alkalinity it is ready for graining. If not, a small quantity of 18° Bé. caustic-soda lye is added and boiled through. This is repeated until the strength holds. By employing this easy test all guesswork in regard to free alka-

linity of lyes is removed. If the free alkalinity is too high, more stock is pumped in and killed.

17. Graining the Soap.—The object of graining is to separate the soap from the glycerine. This is done by adding salt or strong brine. The soap is insoluble in this solution, and on account of its lower specific gravity rises to the top while the lye carrying the glycerine and nearly all the salt falls to the bottom. The kettle is properly grained when a good bright lye drops. There are other salts that will grain; caustic soda and sodium sulphate are among these. Caustic soda is used on rosin changes. Sodium sulphate does not grain as clear as sodium chloride and it requires much more of it. Where reclaimed salt is used, the amount of sodium sulphate formed by the treatment in the glycerine recovery becomes so troublesome that when it reaches 20 to 25 per cent. of the salt, it is used on a first rosin change, and is thus eliminated from the system when that lye is run to the sewer.

Before adding the salt when graining, water enough is added to the kettle to make up the quantity of lye that it has been decided to make. This water is boiled into the soap. A good method of adding this water is to gauge it in time. The pressure from the city mains or from roof tanks that are held at a uniform level is constant enough for this. The instructions are usually given as 10 or 12 minutes of water. This is also done with caustic-lye solutions.

18. An excessive quantity of water in the kettle manifests itself by frothing, and under such conditions dry salt must be used. The nature of the stock used should also be considered. Tallow alone forms a soap that, at this stage, is of a characteristically firm consistency, although fluid.

Soaps made from cottonseed oil, red oil, olive oil, or rosin are very fluid, and from their consistency would seem to indicate the presence of an excessive quantity of water when such is not the case. Coconut oil makes a very fluid soap, and because of the large amount of salt required for graining, the latter should invariably be added in the dry state.

19. With the contents of the kettle boiling quietly, dry salt or saturated brine is added in small quantities at a time and thoroughly boiled through the soap until a portion taken up on a paddle coagulates or separates so that waste lye runs from it. The waste should be clear, of salty taste, and should not contain free alkali in excess of two-tenths of 1 per cent. This amount of free alkali in waste-soap lye is not perceptible to the ordinary taste.

The desired consistency of the grain is a condition arrived at by experience. The use of salt in excess of the amount required to produce this is not only wasteful, but also, if not thoroughly removed in the final settling change, tends to make the soap become fissured, or cracky, in the frames. The amount of salt added will partly determine the degree of hydration of the grained soap.

The more concentrated the salt solution in contact with the soap, the less water will be retained by the soap. With an insufficient quantity of salt, the soap will not be withdrawn entirely from solution. With such a condition, the contents of the kettle on cooling will not present a clean line of demarcation between the soap and the under lye, but there will be an intermediate zone of soft soap. Waste lye withdrawn hot from soap that has been insufficiently grained, will, on cooling, have the consistency of soft soap.

20. In boiling soap of the character under discussion the stock lye should not have a greater density than 13° Baumé, and will contain from 7 to 10 per cent. of salt. The soap is sufficiently grained when a waste lye of this character is withdrawn. It has been found by analysis that this is the lowest density that will remove the soap completely from solution; more salt than this is unnecessary and wasteful. The stock lye is the clearest and least discolored, and, owing to the high percentage of glycerine present, is the most valuable.

21. With the first appearance of a tendency to grain, the quantity of salt added previously should be thoroughly boiled through the soap, and each subsequent addition should be boiled through in the same manner before more is added.

When the desired grain has been obtained, the soap is boiled up to the top of the kettle, and the steam is turned off.

The time allowed for settling after graining depends on how fast the kettles must be worked toward the finish. Usually the kettle is rosined the first or second day after the stock change. This allows at least one glycerine lye to stand overnight. The other glycerine lyes may be drawn 2 hours after the graining is completed.

22. First Rosin Change.—A pure tallow soap has such poor lathering qualities that it needs rosin or oil to make it more soluble. Rosin and oil are used in laundry soap, but oil only, in toilet soap. The rosin is added either directly to the kettle or is saponified alone in another kettle and pumped in. Where the rosin is added directly, the barrels are generally rolled up to the kettle previous to the change being started and all the iron bands but one cut and removed. This is done so that by cutting the last band, the staves and heads fall apart and much time is saved. The rosin is broken into small pieces and shoveled into the kettle.

It is cheaper to use soda ash than caustic for this saponification. A 12° Bé. soda-ash solution is made and brought to a boil, the rosin is shoveled in as in a direct saponification and the whole mass kept boiling until no lumps of rosin are seen on the surface when the steam is shut off. Just before pumping, some dry salt is added to make it pump better. With the use of saponified rosin much less caustic lye is needed for this change. One thousand pounds of rosin requires about 150 pounds of soda ash.

A second rosin lye is pumped in on this change so that the excess of caustic that it contains can be used in dissolving the rosin and also to purify the soap by washing out the color and soluble impurities. The rosin changes are kept well *open* with caustic as very little salt is used. It is boiled thoroughly and always stands overnight so as to get out all the impurities possible.

23. Second Rosin Change.—The main object of the second rosin change is to insure complete saponification. The

boiled-up niger is added to fill up the kettle and reclaim all the good soap possible. All rosin changes are very tricky in their boiling and require all the skill of the soap boiler in getting a good mixing of all the ingredients. The steam is put on for a short while and the kettle watched very closely. The steam has a tendency to hold in pockets and break through with such violence as to jump out of the kettle. By putting on and shutting off the steam until it begins to break through quietly, a gentle boil may be had.

On the addition of alkali, as previously noted, the soap is well boiled through simultaneously with the addition of the rosin. Combination ensues quickly. The same care should be taken to insure the fullest absorption of the alkali, with the least amount added in excess to be discharged into the rosin lye.

During this change, combination is greatly assisted by keeping the contents of the kettle in a state of partial precipitation by the addition of caustic-soda lye. In the language of the soap boiler, this is termed either *graining the soap with alkali,* so called from the consistency that the soap assumes, or *keeping the soap open on alkali,* by which is meant not allowing the soap to *close* or *flatten,* or to lose its grainy appearance on passing into complete solution. *Opening the soap,* therefore, means partly precipitating it by the addition of a body in whose solution it is insoluble.

24. The rosin lye is nearly always very highly colored, with a depth of color depending largely on the quality of the rosin used. On the stock change, 31,000 pounds of mixed stock was killed. This admixture will carry well one-half its weight, or 15,500 pounds, of rosin—roughly, 36 barrels. After the withdrawal of the rosin lye there will remain in the kettle about 70,000 pounds of soap.

25. Strong Change.—The strong change is boiled on water if there is enough alkali left from the second rosin change, or with 4° to 5° Bé. caustic lye if it appears weak. The soap which has flattened out with the water will open very slightly so as to drop only a small quantity of slimy lye.

This change is boiled slowly, which tends to make the contents of the kettle homogeneous.

26. The purpose of the strengthening change is to complete the saponification and to discharge the salt, coloring matter, and other impurities retained mechanically by the soap. No salt is used for graining on this change. The 2 to 4 per cent. of salt commonly present in strengthening lyes represents the amount that has been retained mechanically by the soap and washed from it on this change.

The alkali wash promotes the discharge of the coloring matter, and completing the saponification of the last traces of unkilled stock also assists very materially in the development of the texture desired in the finished product.

27. Settling the Soap.—*Finishing* or *settling* the soap consists essentially in thinning the soap to the desired consistency with either weak lye or water. The water may be added during boiling or it may be derived from the steam condensed during this change. The strengthening lye from the preceding change is withdrawn and the soap is boiled up with live steam. Water is added in small quantities at a time until the soap is closed.

The boiling on the *settle* is done very slowly and may take all day to bring it into a condition that satisfies the soap boiler. Good soap can never be harmed by too much proper boiling.

Some free alkali is retained mechanically by the soap after the withdrawal of the strengthening lye. This amount is sufficient to impart a slight sharpness or alkalinity to the settled soap. It is claimed by some manufacturers that the soap should be settled in a perfectly neutral condition; others claim that the best results are obtained with a slight sharpness present.

28. The soap is boiled up to the top of the kettle and is then allowed to stand for about 6 or 7 days, during which time the contents of the kettle, by virtue of the different specific gravities, resolves itself roughly into two portions, namely,

the finished soap, carrying about 30 per cent. of water (this proportion, however, varying with the grain of the finish),

TABLE II

ANALYSIS OF SOAP DURING SETTLING PERIOD

	When Steam is Shut Off Per Cent.	After 12 Hours Per Cent.	After 60 Hours Per Cent.
Free $NaOH$	.15	.02	Trace
Free Na_2CO_3	.22	.13	.11
Salt	2.54	.77	.40
Water	45.58	32.82	30.40

and the niger, which carries considerably more water than does the supernatant soap, as well as the impurities and coloring matter settled from the latter. The settling change is a very important one, for on its proper operation depends the success or failure of the boil of soap. The length of time allowed to settle a boil, varies. It is best when permitted to stand a week. However, in the busy seasons it can be

TABLE III

ANALYSES OF NIGERS OF SETTLED ROSIN SOAP

	1	2	3
Water	59.14	66.29	55.86
Fatty and rosin anhydrides	30.41	23.27	35.83
Combined alkali	3.92	3.16	4.36
Free $NaOH$	.70	1.02	.86
Free Na_2CO_3	.56	.56	.58
Salt	2.34	3.24	1.71
Undetermined	2.93	2.46	.80
	100.00	100.00	100.00

crutched and framed on 4 or 5 days' settling. The settles of the same day are usually framed in the order of their temper-

atures, the coolest one being taken first. If one a day earlier than its schedule is needed, the coolest one is also framed first.

29. Niger.—The liquor from the settled soap is called the *niger*. It contains the impurities and constitutes from 20 to 25 per cent. of the volume of settled soap in the kettle. This proportion varies with the degree of hydration of the finished soap, the length of time allowed for settling, and the temperature of the mass. Analyses of the principal components of typical nigers are given in Tables III and IV.

The more thinly the soap is finished, the larger will be the niger, and the impurities of the finished soap, other things being equal, will be more completely settled into it. Care should be taken not to finish the soap too thinly, for the excessive quantity of water added to the kettle not only makes the finished soap softer, but leaves a large bulk of niger to receive subsequent treatment.

TABLE IV

ANALYSIS OF NIGER OF A TOILET SOAP

Water	70.83
Fatty anhydrides } Combined alkali }	22.65
Free $NaOH$	.78
Free Na_2CO_3	.80
Salt	3.76
Undetermined	1.18
	100.00

30. On the other hand, a soap finished too closely, owing to the addition of an insufficient quantity of water, will separate the impurities very incompletely and yield a small niger. Other conditions being satisfactory, the longer the settling period, the more complete will be the separation of impurities, with the formation of a niger of proper volume. If, during this period great attention is not given and the soap is allowed to cool too quickly, which is often the case with a small kettle or with one exposed to the weather, especially in winter, separation of the impurities will be checked by a local or general cooling of the mass, and the niger will remain distributed unequally throughout the soap. This is overcome by insulating the kettle.

31. The settling change is not primarily a purifying change, but provides first for the production of a mass of a certain appearance and consistency, and when this is obtained and the proper conditions just noted are observed, the soap mass separates the impurities, thus forming the niger.

The soap mass is said to be finished fine or coarse, or, respectively, hard or soft, according to its degree of hydration. The condition described as fine or hard obtains when the soap taken up on the paddle and held in a slanting position falls from it in short, small flakes and cools rather quickly. The condition described as coarse or soft obtains when the soap falls from the paddle in large flakes and cools less quickly. The appearance and consistency must be learned by actual experience, by personal handling of the material itself. The process of clarification can be noted on the top of the kettle as soon as the final steam is shut off.

32. Filling of Soap.—The detergent qualities of soap are greatly increased by the addition of certain substances in aqueous solution while the soap is in a fluid state.

Borax and sodium carbonate are employed, but the use of the former for this purpose is, as a rule, displaced by the cheaper alkaline carbonate.

As all surface water contains mineral salts, chiefly the carbonates and sulphates of lime and magnesium, it is necessary to neutralize these before the soap can exert any cleansing action. Insoluble soaps of lime and magnesium are formed by the combination of soluble soaps and the salts just mentioned, which impart the so-called hardness to surface water.

Sodium carbonate is a valuable addition to a soap, as a more economical use of soap is effected by its incorporation, as will be described subsequently. The carbonate effects the neutralization of mineral salts, thus leaving the soap to exert its legitimate cleansing action. The value of sodium carbonate to increase the detergence of soap was early recognized, as was also its property of hardening the soap, thus permitting the incorporation of more water than would be possible without its use.

Sodium silicate lends itself readily to incorporation with fluid soap, as it possesses very little detergent power. It is primarily a cheapener and imparts a smooth appearance to the finished soap, which becomes extremely hard on drying.

33. Sodium carbonate and sodium silicate are the chief filling agents. Their use in soap in large or small amounts is determined by the grade desired to be made and gives rise, respectively, to the terms *heavily filled* and *lightly filled.*

Mineral soap stock is a residuum from petroleum distillation that is frequently used in heavily filled soap. This stock

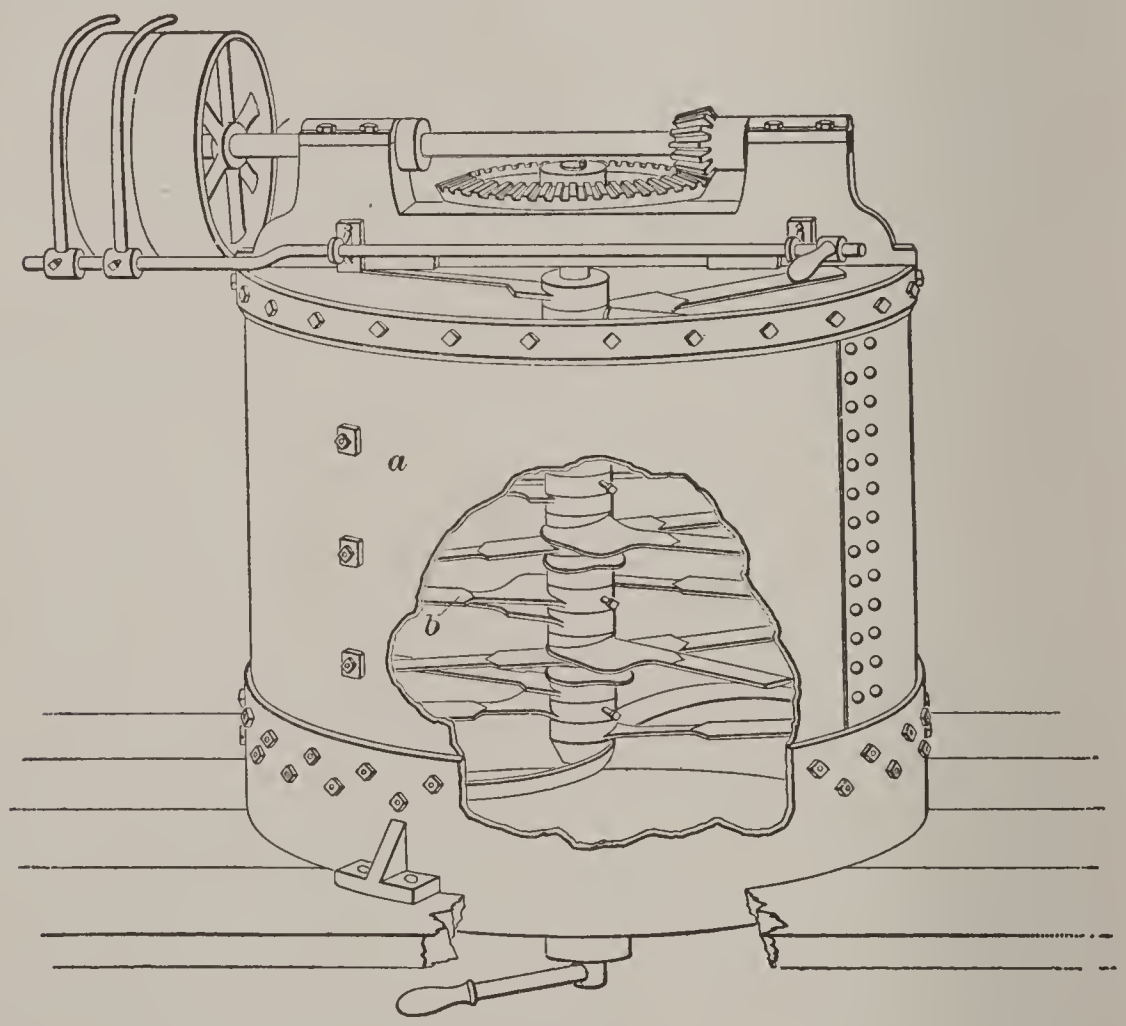


FIG. 6

imparts a smooth appearance to such soap, and thus counteracts the tendency of the mineral salts mentioned to grain the soap when added in large amount.

The limit to the use of filling agents is determined by the intelligence of the consumer. The incorporation in soap of filling agents is not, strictly speaking, an adulteration, so

long as the product is sold at a price commensurate with its quality.

34. Crutching the Soap.—For the incorporation of filling material into soap, the belt-driven crutcher is generally employed. There are three styles of this machine, each of which possesses several points of excellence.

Style A, shown in Fig. 6, consists of a cylindrical vessel *a*, in which is mounted a vertical shaft carrying a series of horizontal paddles *b*. These paddles rotate entirely within the body

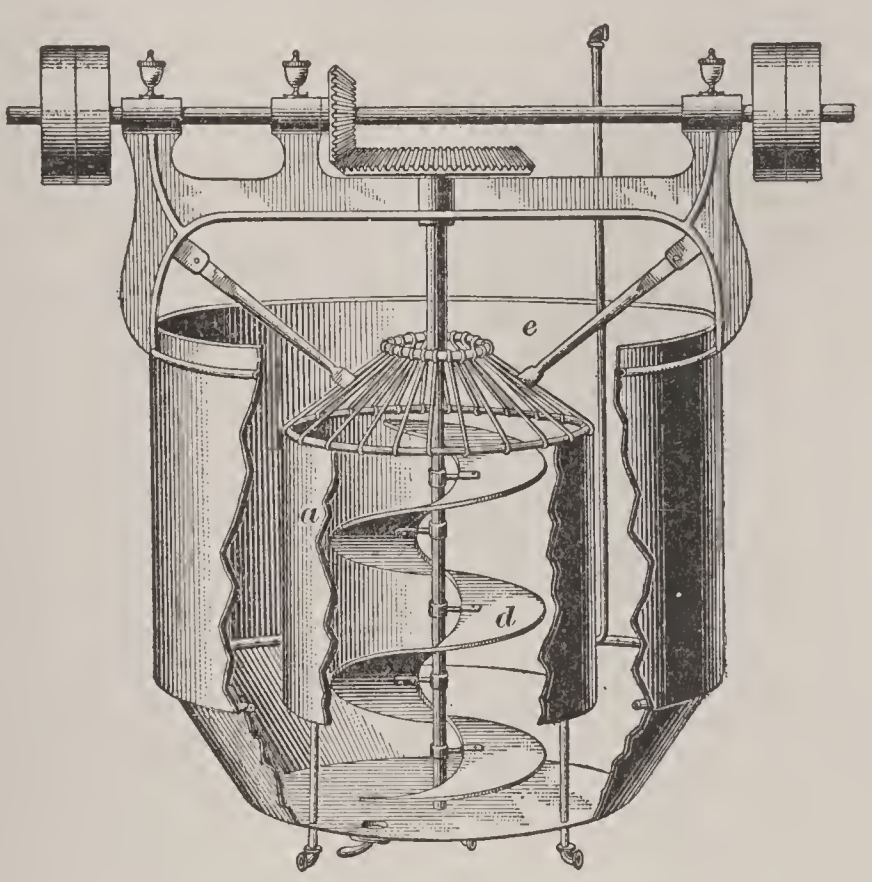


FIG. 7

of the soap, which remains practically stationary. The blades of the horizontal paddles may be so constructed, however, as to impart an upward movement to the soap. With a crutcher constructed as shown in Fig. 6, it is impossible to incorporate air into the mass of soap, as the mixing is done entirely within the body of the soap.

35. The distinguishing feature of the crutcher known as style B, shown in Fig. 7, is an inner concentric cylinder *a*, enclosing a broad Archimedean screw *d* mounted on a vertical shaft. Both the outer shell *e* and the concentric cylinder *a*

may be steam-jacketed or water-jacketed or fitted for both. This style is more commonly used without the steam jacket.

With this crutcher, the entire mass of soap may be moved from below upwards through the central cylinder by means of the screw *d,* and downwards between the outer shell *e* and the concentric cylinder *a,* or in the reverse direction, according as the belt is advanced or reversed.

36. Style C, shown in Fig. 8, is essentially the same as style A. The shaft of this crutcher is horizontal, with blades

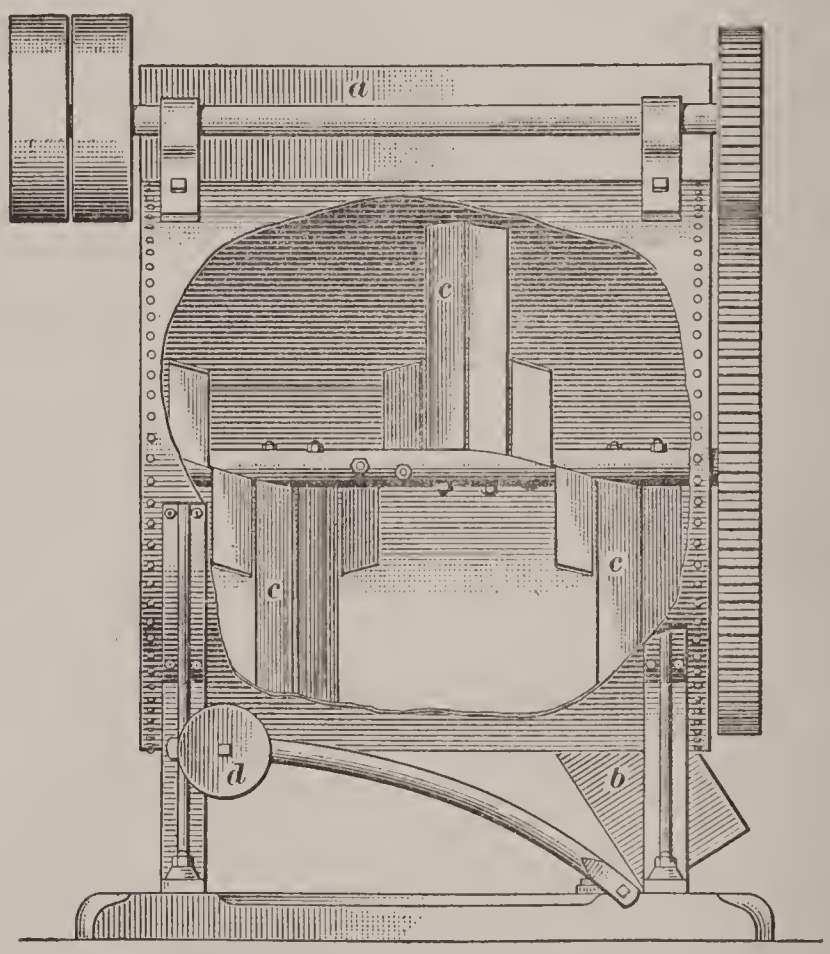


FIG. 8

of even or varying length mounted in screw-like fashion on it. Soap is pumped or dropped into the hopper *a* until the paddles *c* are covered to a depth of 2 inches. The crutcher is then started and run until the soap is crutched. The screw-like motion of the paddles works the contents of the crutcher toward the outlet *b,* which is closed by the counterpoise *d.* If the soap is not too thick, it will flow freely from the outlet *b.* If too thick, it is necessary to start the crutcher.

Each type of crutcher may be steam-jacketed or water-jacketed or both if desired. In factories that are not equipped with a separate remelter, this feature is essential. The steam-jacketed crutcher can then serve as a remelter. The capacity

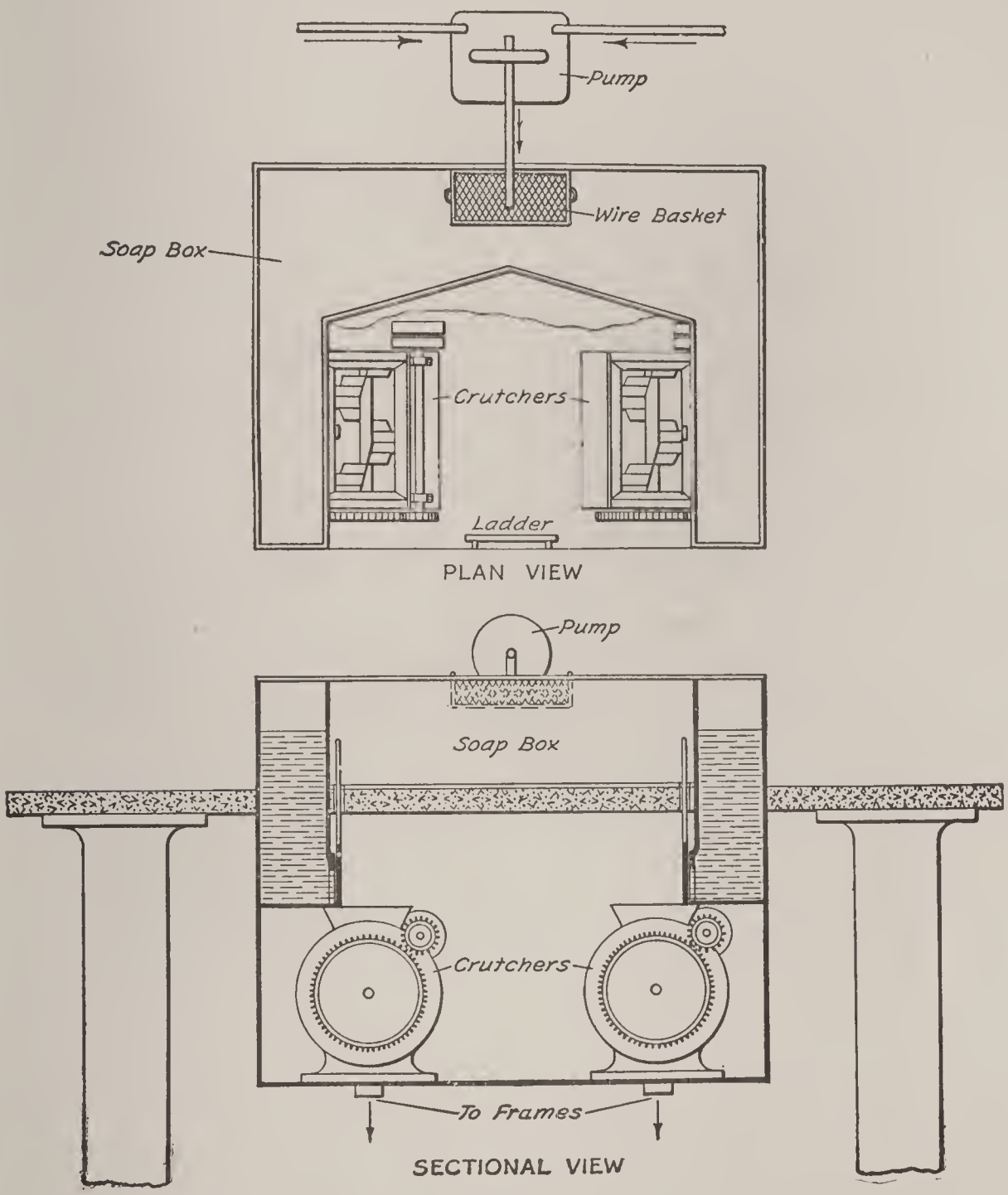


FIG. 9

of a crutcher is that of one frame, namely, 1,200 pounds. The crutchers are sometimes hung between floors in a cage or pit. It is the general practice to decide on a set temperature at which to drop each frame of the same class. A temperature of 142° to 145° F. is very good for the soap just described.

37. The use of the remelter is gradually growing less. It is much easier and cheaper to arrange the crutchers as shown in Fig. 9. This allows all clean scrap from the cutting tables to be added to the fresh soap going to the crutcher, where it serves a two-fold object. First, it is worked back into a finished form; and second, it cools the hot soap to the desired temperature. With well-insulated kettles, the soap crutching is seldom under 160° F. in winter and 170° to 185° F. in summer, and its temperature can be entirely controlled by the use of scrap so that water in the jackets is seldom used to get the temperature desired before dropping.

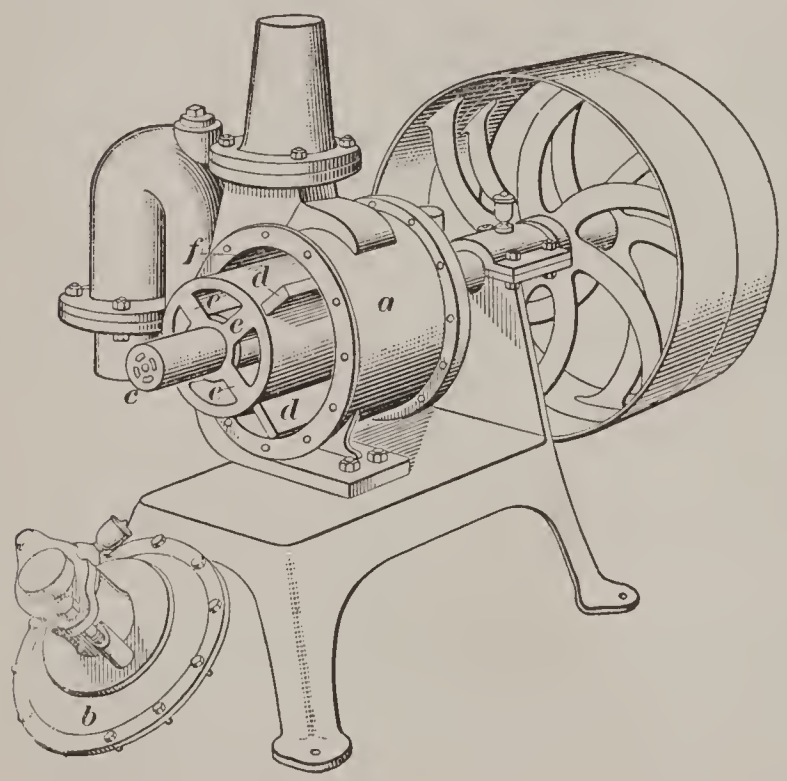


FIG. 10

Soap is pumped to the box, which is fitted with a heavy strainer, usually a wire basket. The amount of scrap that experience has determined to be proper, is added to the hot soap and stirred in with a paddle. As most of this scrap comes fresh from the slabber and cutting tables, it softens quickly. When the charge has been taken into the crutcher, the crutching is continued until the whole mass is homogeneous and shows no signs of the scrap soap used. It takes 10 to 12 minutes to accomplish this. This work proceeds so regularly that it is usually controlled by the clock.

38. Floating Soap.—With all other classes of soap, the crutcher is always filled well above the paddles or blades to exclude carefully all air. It is desirous to make ordinary laundry soap as dense in structure as possible. In making floating soap, however, this procedure is reversed and the

specific gravity is lowered by the incorporation of minute air bubbles.

To accomplish this, the crutcher is filled to within 6 to 10 inches of the top and covered, and the crutching continued until the soap has swollen to some predetermined height.

39. Soap Pumps.—The liquid soap is transferred to the crutcher by means of a pump. The pumps used vary some-

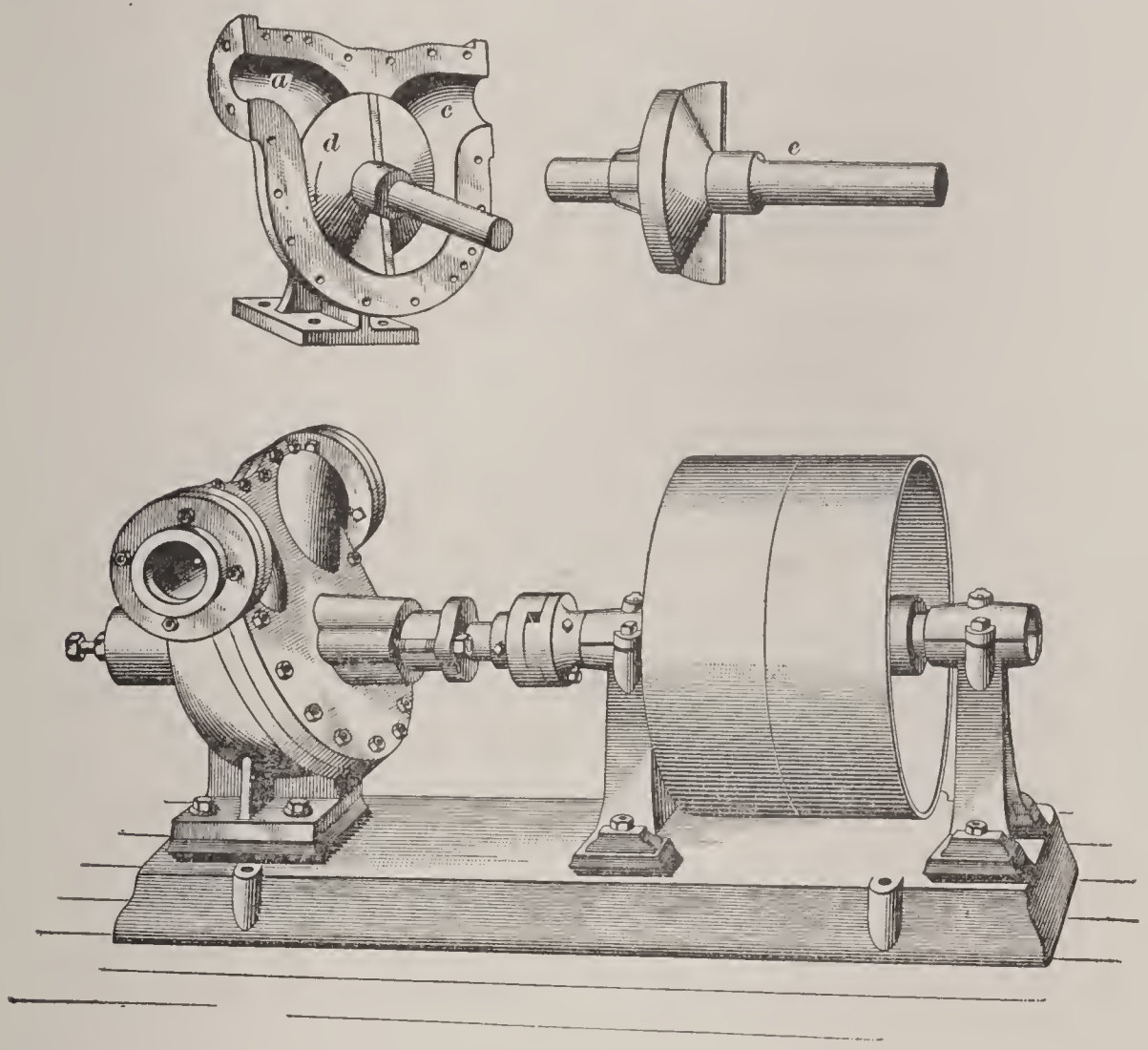


FIG. 11

what in construction, and only those most generally used will be described.

In the Tabor rotary pump, the working parts of which are shown in Fig. 10, *a* is the shell, or case, of the pump; *b* is the head that covers the end of the shell; *c* is the piston that carries the valves; *d* are the valves that pass through the piston in the ways *e*, and as the piston revolves, they pass in and out, back and forth through the piston, following the inside lines of the shell. The piston sets tightly against the shell at the

point *f*, between the point of suction and discharge. Rotating the piston creates a vacuum in the suction pipe, and the pump is thus set into operation.

40. The Hersey rotary pump, shown in Fig. 11, consists essentially of a cone-shaped casting, or piston, *d*, carrying blades, the whole being mounted on the end of a shaft *e*. The piston rotates in a specially shaped case, and when it turns in the direction indicated by the arrow, suction takes place at the orifice *a* and discharge at *e*. The reverse occurs when the piston is rotated in the opposite direction.

41. The Johnson rotary pump, shown in Fig. 12, consists of an outside shell *a*, with suitable parts *b* and *c* for connecting

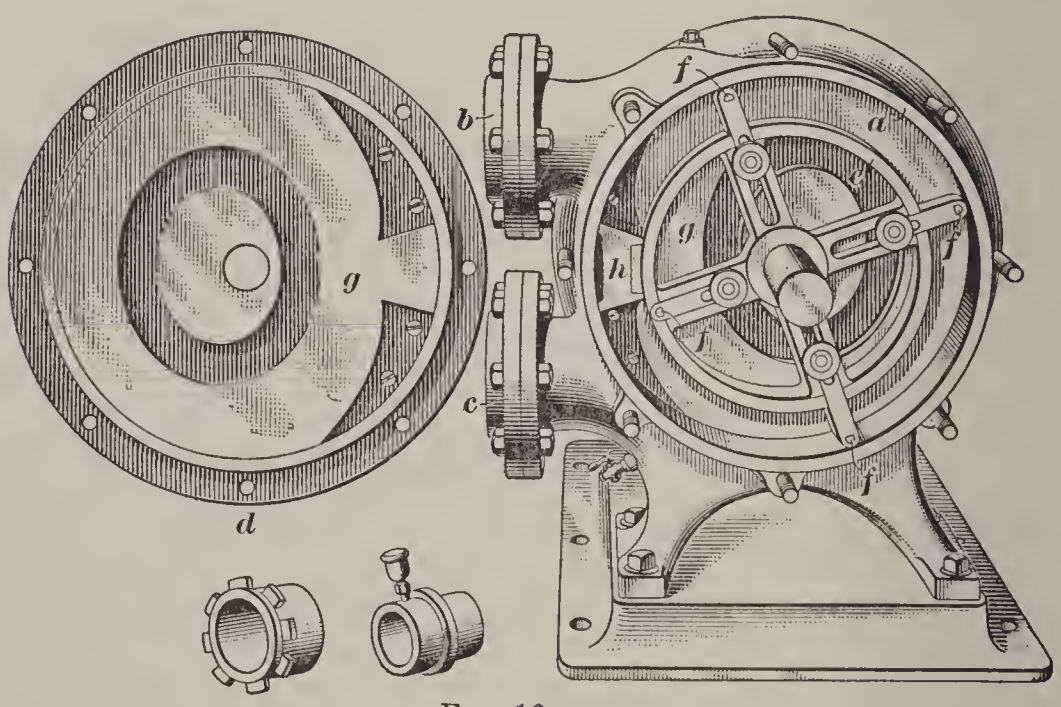


FIG. 12

suction and discharge pipes; two side plates, one of which is shown at *d*, with the cam *g*, and inside of all a circular casting, or piston, *e*, in which are held the piston heads *f* operated by the cam *g*. As the piston revolves, the cam *g* causes the piston heads *f* to move in and out of their ways, being at their extreme positions as shown in the figure. The block *h* separates the suction and discharge chambers.

42. The rotary type of pump is adapted for a variety of uses in the soap factory. Its simple construction, ease of

operation, and freedom from expensive repairs give it many advantages over the ordinary steam pump. The chief uses for a pump are to transfer stock and caustic lye to the soap kettle, the finished soap to the crutcher, and waste-soap lye to the glycerine refinery. Large plants are usually laid out so that as much work as possible can be done by gravity. As a rule, all glycerine lyes, caustic-soda lyes, and sal-soda solutions are handled in this manner.

43. On the discharge side of the pump there should be connected a steam pipe that will serve to blow out and clean the interior of the pump and the discharge pipe after use. As shown in Figs. 10 and 11 the pumps are provided with tight and loose pulleys, on the latter of which the belt may be shifted when the pump is not in use.

For pumping the soap from the kettle to the crutcher, the pump should be placed below the level of the draw-off pipe in the kettle, and the outlet, or discharge, pipe should be of slightly smaller diameter than the intake pipe. In this way gravity will aid the feed and provide for a steady discharge. The rotary, belt-driven pump represents a great improvement in productive economy over the old-time ladle and bucket as an instrument for transferring soap from vessel to vessel.

FILLING MATERIALS

44. Soda Ash.—The most valuable material to be added to laundry soap is soda ash. This material is introduced into the crutcher in the form of a saturated solution. The crutcher room is usually provided with a steam-heated kettle having an agitator for dissolving the soda ash as required. During the afternoon of the day previous to crutching, a quantity of solution sufficient for the entire boil of soap is made up.

When the arrangement of the factory permits, the sal-soda boiling tank is placed beside the caustic-soda lye tank on the soap-boiling floor. Another small tank is put on the crutching floor into which the sal-soda solution is drawn for use as needed. This serves to hold as much heat as possible in the

main solution. The amount of sal-soda solution is usually weighed for each crutcher charge of soap.

45. With a soda-ash kettle of given capacity, the quantity of soda ash and water necessary to produce a solution of the required density is easily ascertained by experience. The mixture is boiled with open steam to a density of 33° Baumé while hot. During the night the impurities in the solution, introduced by the soda ash, will have settled to the bottom and the solution will have cooled to a temperature of about 140° F., with the specific gravity increased to 36° Baumé. A solution lower than this in specific gravity should not be used in filling a soap.

The draw-off pipe should be placed 2 or 3 inches above the bottom of the sal-soda kettle, so as to avoid the removal of the settled impurities.

46. The quantitative properties of sodium-carbonate solutions above a density of 18° Baumé are determined at a temperature of 30° C. At a temperature of 15° C., solutions of the density shown in Table V (B) will crystallize, forming the hydrated salt, $Na_2CO_3 \cdot 10H_2O$, or $Na_2CO_3 10Aq$ (Aq. is the abbreviation for the word *aqua,* meaning *water*) as it is more frequently written, commonly known as *sal-soda.*

47. Concentrated solutions of sodium carbonate, when added in large amounts to any soap and particularly to soap made from soft stock, which, as known, sweats more readily than soap made from firmer stock, will soon cause the soap to effloresce. This is a most disagreeable property and detracts greatly from the appearance of the product. Also, when added in greater quantity than the soap can assimilate, the soda ash tends to grain the soap. With heavily filled cheap soaps, this condition represents the limit of the addition; soda ash and other filling agents possessing detergent properties then become adulterants.

48. Borax.—The addition of borax to soap is desirable, as this material is a mild alkali and possesses all the advantages of soda ash with none of its caustic properties. Owing to the

TABLE V

SPECIFIC GRAVITIES OF SOLUTIONS OF SODIUM CARBONATE (LUNGE). (A) AT 15° C.

Specific Gravity	Degrees Baumé	Degrees Twaddell	Per Cent. Na_2CO_3	Per Cent. Na_2CO_3 10 *Aq.*	1 C. M. Contains Kg.	
					Na_2CO_3	Na_2CO_3 10 *Aq.*
1.007	1	1.4	0.67	1.807	6.8	18.2
1.014	2	2.8	1.33	3.587	13.5	36.4
1,022	3	4.4	2.09	5.637	21.4	57.6
1.029	4	5.8	2.76	7.444	28.4	76.6
1.036	5	7.2	3.43	9.251	35.5	95.8
1.045	6	9.0	4.29	11.570	44.8	120.9
1.052	7	10.4	4.94	13.323	52.0	140.2
1.060	8	12.0	5.71	15.400	60.5	163.2
1.067	9	13.4	6.37	17.180	68.0	183.3
1.075	10	15.0	7.12	19.203	76.5	206.4
1.083	11	16.6	7.88	21.252	85.3	230.2
1.091	12	18.2	8.62	23.248	94.0	253.6
1.100	13	20.0	9.43	25.432	103.7	279.8
1.108	14	21.6	10.19	27.482	112.9	304.5
1.116	15	23.2	10.95	29.532	122.2	329.6
1.125	16	25.0	11.81	31.851	132.9	358.3
1.134	17	26.8	12.61	34.009	143.0	385.7

(B) AT 30° C.

Specific Gravity	Degrees Baumé	Per Cent. Na_2CO_3	Per Cent. Na_2CO_3 10 *Aq.*	1 Liter Contains Grams	
				Na_2CO_3	Na_2CO_3 10 *Aq.*
1.308	34	27.97	75.48	365.9	987.4
1.297	33	27.06	73.02	351.0	947.1
1.285	32	26.04	70.28	334.6	902.8
1.274	31	25.11	67.76	319.9	863.2
1.263	30	24.18	65.24	305.4	824.1
1.252	29	23.25	62.73	291.1	785.4
1.241	28	22.29	60.15	276.6	746.3
1.231	27	21.42	57.80	263.7	711.5
1.220	26	20.47	55.29	249.7	673.8
1.210	25	19.61	52.91	237.3	640.3
1.200	24	18.76	50.62	225.1	607.4
1.190	23	17.90	48.31	214.0	577.5
1.180	22	17.04	45.97	201.1	542.6
1.171	21	16.27	43.89	190.5	514.0
1.162	20	15.49	41.79	180.0	485.7
1.152	19	14.64	39.51	168.7	455.2
1.142	18	13.79	37.21	157.5	425.0

higher cost, its use in soap manufacture is limited; with certain brands, only sufficient is used to justify in a measure the title given to the soap.

49. Sodium Silicate.—Next to soda ash, sodium silicate, commonly called *water glass* or *soluble glass,* is the most extensively used filling agent. Its consistency lends itself to ready incorporation with the semifluid soap. It possesses detergent power, and when used with due regard to the price of the finished soap, it is a valuable addition to the ordinary household soap.

Sodium silicate is made by fusing pure white sand and soda ash in a reverberatory furnace, such proportions being used that the resulting glass can be expressed by the formula $Na_2O \cdot 4SiO_2$. The resulting glass is broken into fragments and introduced into a digester that is already charged with an amount of water to yield a solution of any density desired, and high-pressure steam is then admitted. When solution is complete, the contents of the digester is run into barrels, in which shape it is received by the soap maker.

50. Sodium silicate is generally used at a density of 40° Baumé, in which condition it has the consistency of thick molasses, is transparent, and hardens quickly on exposure. At ordinary temperatures it will flow readily from the barrel. It must be in a fluid condition when used. In cold weather it may be softened by blowing steam into the barrel. If the head of the barrel is removed and the contents exposed to the air, those varieties deficient in alkaline strength will *jelly,* or separate free silicic acid through the displacement of the latter acid by the stronger carbonic acid of the atmosphere. This may be overcome by stirring up the mass with strong caustic-soda lye, thus effecting a combination of the silicic acid with alkali.

51. When intended for the use of soap makers, the sodium silicate has an average composition as follows: Water, 62.8 per cent.; SiO_2, 28.7 per cent.; Na_2O, 8.5 per cent. The more silicic acid the product contains, the more difficult it will be to dissolve it in water. The composition

of commercial sodium silicate, as it occurs in solutions of different densities to be used for different purposes, is variable, depending on the proportions of soda ash and silica used in the original charge and on the amount of water in which the fused mass is dissolved in the digester. There is practically no neutral silicate; that which is called neutral contains an excess of silicic acid, although it is not acid to litmus.

52. On aging, soap filled with sodium silicate becomes very hard. When well mixed with the soap, a reasonable proportion of sodium silicate greatly improves the appearance and enables a larger quantity of sal-soda to be carried without the efflorescence that would soon be produced without its use.

While sodium silicate possesses detergent properties, it is used primarily as a cheapener. By the use of suitable proportions of solutions of soda ash and sodium silicate, the quality of laundry soap is greatly improved. The soap is made more durable from the hardness produced by the crystallization of the salts; also the rapid drying of the soap is retarded.

When used in excess in cheap soap, the salts not only permit the absorption of a larger amount of water than would otherwise be practicable, but also, when used in soap made from soft stock, they impart a firmness that, without their use, would not be possible without having previously transformed the product into a variety of boiled-down soaps.

53. Miscellaneous Fillers and Adulterants.—Ground quartz, or silica, marble dust, mineral soap stock, a petroleum residuum, starch, and talc may be mentioned as fillers. They are adulterants pure and simple.

54. Perfuming the Soap.—With the best grades of laundry soap, it is common practice to add a small amount of either a single essential oil or a mixture of oils in order to produce a pleasant and lasting perfume. The quantity added is seldom in excess of $2\frac{1}{2}$ pounds per frame. The selection of the oil or mixture of oils is best determined by experiment, the object being to choose an oil or mixture

of oils that will best counteract the resinous odor inseparable from rosined soaps. Too much care cannot be used in selecting a perfume for a soap, because, in many cases, the users identify the soap by its perfume.

55. Crutching the Filler and Perfume Into the Soap. The temperature best adapted to crutching depends largely on the character of the stock used in the soap and on the quantity and temperature of the filling material added in the crutcher. The temperature of crutching need not be so high for soap made from soft stock, because of its natural softness, as for soap made from firm stock.

If the crutcher is provided with a steam jacket, the soap can be easily kept at any desired temperature. Such devices, however, entail the use of a large amount of steam, and, moreover, for this purpose are not absolutely essential, but desirable. It is best and of great advantage to add the soda-ash solution at the same temperature as that of the soap, and when prepared as has been previously explained, it will be at the proper temperature when the soap is ready to crutch.

56. When ready to crutch, the swing-joint pipe is lowered a short distance below the level of the soap in the kettle and held in place by a chain, as shown in Figs. 3 and 4. The rotary pump is started and the crutcher is filled. When approaching the line at which the niger usually shows, the swing joint is watched very carefully and lowered a little at a time, just enough to keep the pump from sucking air.

The speed of crutching is best determined by experience. For a soap of the character under discussion, 80 pounds of sal-soda is run in and the mass crutched until fairy homogeneous. The sodium silicate is then added and crutched in. The perfume is added last, about 2 minutes before dropping, so as to avoid loss from the hot soap, and the soap is crutched until a portion removed on a paddle is perfectly homogeneous in texture and smooth in appearance.

Under satisfactory conditions, from 10 to 12 minutes is sufficient to crutch a frame of soap. With completely saponified soap that is pumped into the crutcher at a temper-

ature not exceeding 160° F. in winter and that carries a reasonable amount of filling, no trouble need be experienced in crutching. The primary conditions for satisfactory work are that the stock shall be completely saponified and the soap well settled. As to the soap being neutral or having a slight sharpness, there is a difference of opinion.

57. At the end of the crutching period, the outlet in the bottom of the crutcher is opened and the contents is emptied into a frame standing on the floor immediately below the crutcher. Where it is possible to operate two crutchers,

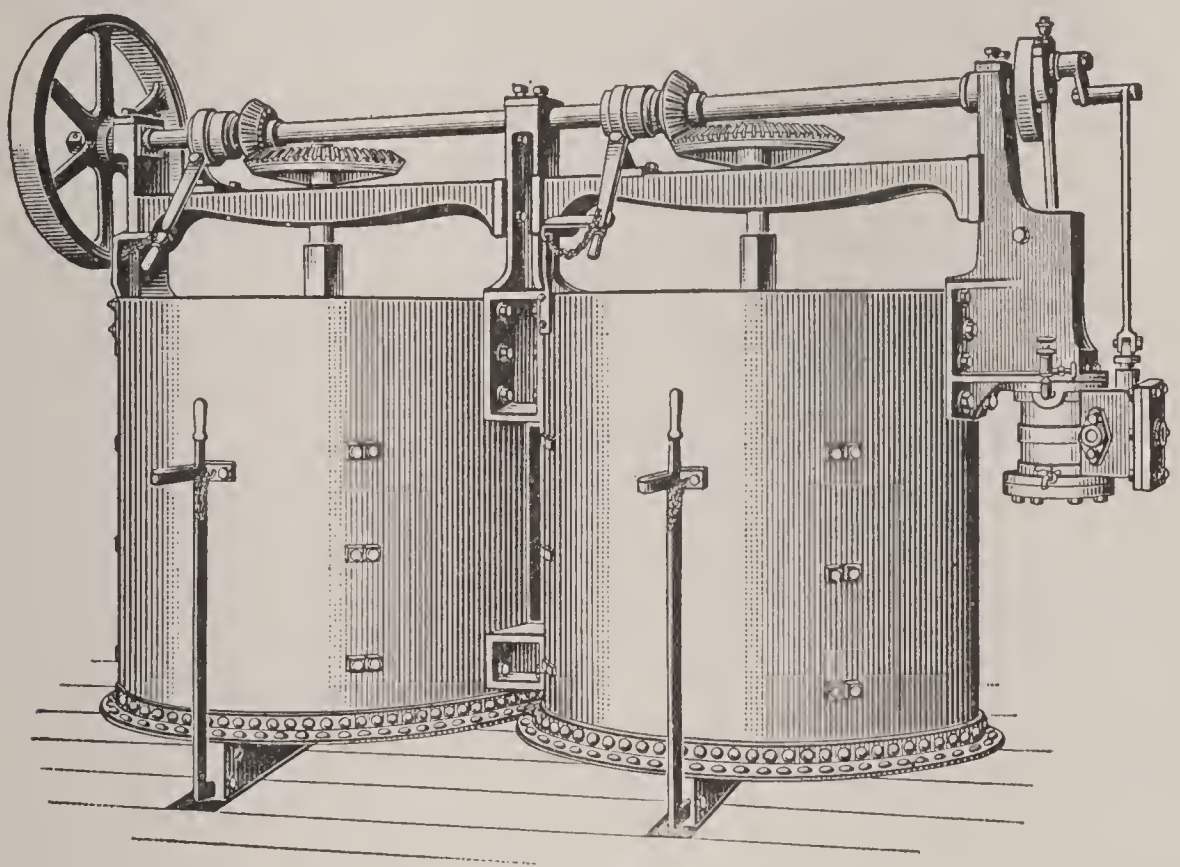


FIG. 13

mounted as shown in Fig. 13, the work is greatly facilitated, as the crutching can proceed in one while the other is being emptied, and vice versa. The man in charge of crutchers can always tell when the niger is reached. The appearance of the soap changes very decidedly; it becomes dark, thin, and streaky. By allowing it to flow across a trowel or paddle, the change is caught almost at once. The pump is shut off and the niger in the pump and line steamed back into the kettle. The niger is boiled up and pumped into any waiting second rosin change. The kettle is then ready for a fresh charge of stock.

FINISHING-ROOM PROCESSES

58. Framing the Soap.—The soap frame, shown in Fig. 14, has attained its present shape and size as the result of experience in handling soap at this stage of its manufacture. This frame consists essentially of an uncovered box with removable wood or sheet-steel sides, and with ends of wood or sheet steel set on a wooden bottom, which is mounted on truck wheels. It has a capacity of 1,000 to 1,200 pounds.

There are various styles manufactured, all with the single aim of producing a box that can be readily put together and taken apart, that will be durable, as light in weight as is

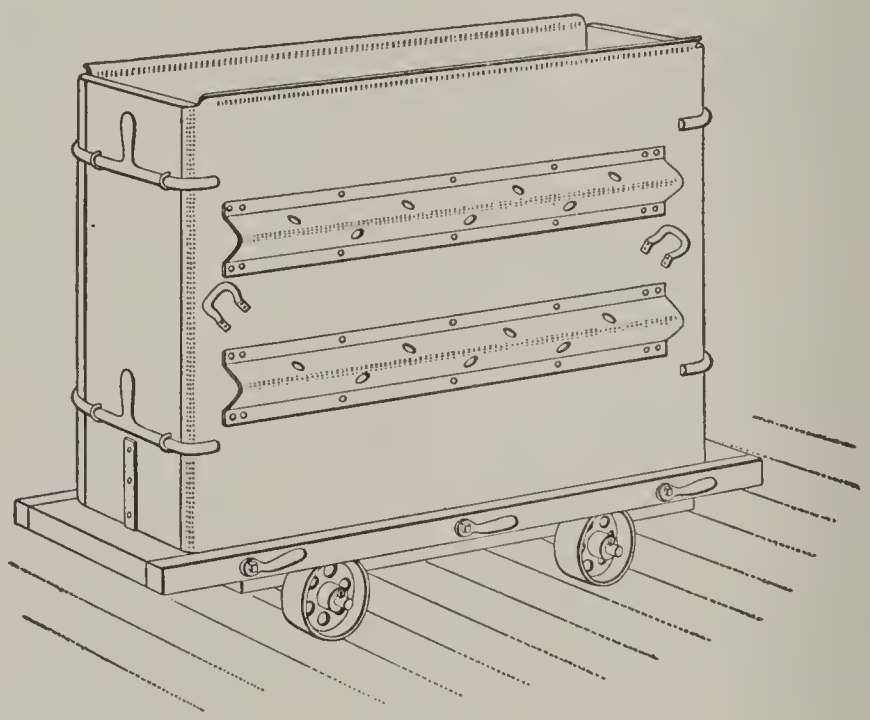


FIG. 14

consistent with strength, that can be easily moved about, and that will possess the most important qualification—tightness. The dimensions of the frame are variable and are determined, especially the width, by the size of the bar into which the slabbed soap is to be cut, it being the aim to keep the percentage of scrap at the cutting table as low as possible.

In the frame-room equipment, it is best to have an extra bottom for each frame. The sides of a frame may be removed after the soap has cooled sufficiently to permit this, and then mounted on the extra bottom. This is a most economical method, the usefulness of the frame being doubled, as the

original bottom carries the soap through the slabber and to the cutting table, by which time the original sides may be used to enclose a new frame of soap.

59. Previous to crutching, or as it proceeds, a sufficient number of frames are put in readiness. When the crutchers are operated in pairs, an empty frame should stand ready to receive its charge as the preceding one is being filled. The filled frame, with the soap smoothed down into the edges of the frame by means of a short paddle and heaped up longitudinally in the middle, is pushed into its stand in the frame room. Here it is allowed to remain for a varying period, usually from 3 to 5 days, which period is determined by the demands of the factory, the season, the character of the soap, and the temperature at which it was framed.

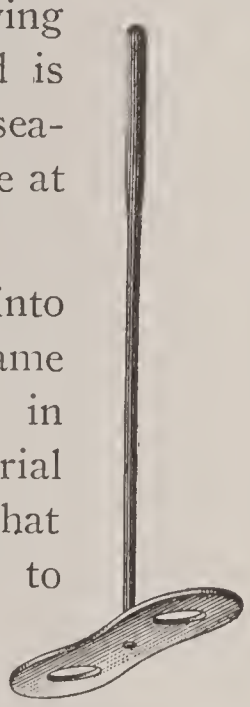


FIG. 15

60. Before the steam-driven crutcher came into use, the soap was laboriously crutched in the frame with a *hand crutch*. The hand crutch, shown in Fig. 15, is still in use to prevent the filling material from settling to the bottom of the frame in soap that was crutched at too high a temperature; to distribute the material used to produce a mottle; or to distribute the reduction of temperature uniformly throughout the entire mass as cooling proceeds, thus preventing the separation of the softer from the harder soap.

With soap made from tallow, cottonseed oil, or grease, and rosin, and filled as has been noted, the sides may be removed from the frame on the second day after crutching. After removing the frame sides, the sides of the soap are scraped so as to remove any stains and blotches of adhering matter that may be present, and the soap is then ready to be slabbed.

61. Slabbing Machine, or Slabber.—The device known as the *slabbing machine,* or *slabber,* varies greatly in simplicity and cheapness of mechanical construction. It is a development of the old hand method of drawing a wire in parallel lines longitudinally through the mass of soap. In the machine

slabber, whether hand- or power-driven, the direction of application of the power is reversed, the frame of soap being forced through a series of parallel wires arranged on a framework to the height of the soap to be slabbed. The essential mechanical features of the machine slabber are shown in Fig. 16.

The power-driven slabber is automatic in action. The frame is run into the cage and the cutting head locked into place. The cutting head travels through the soap and returns, pushing

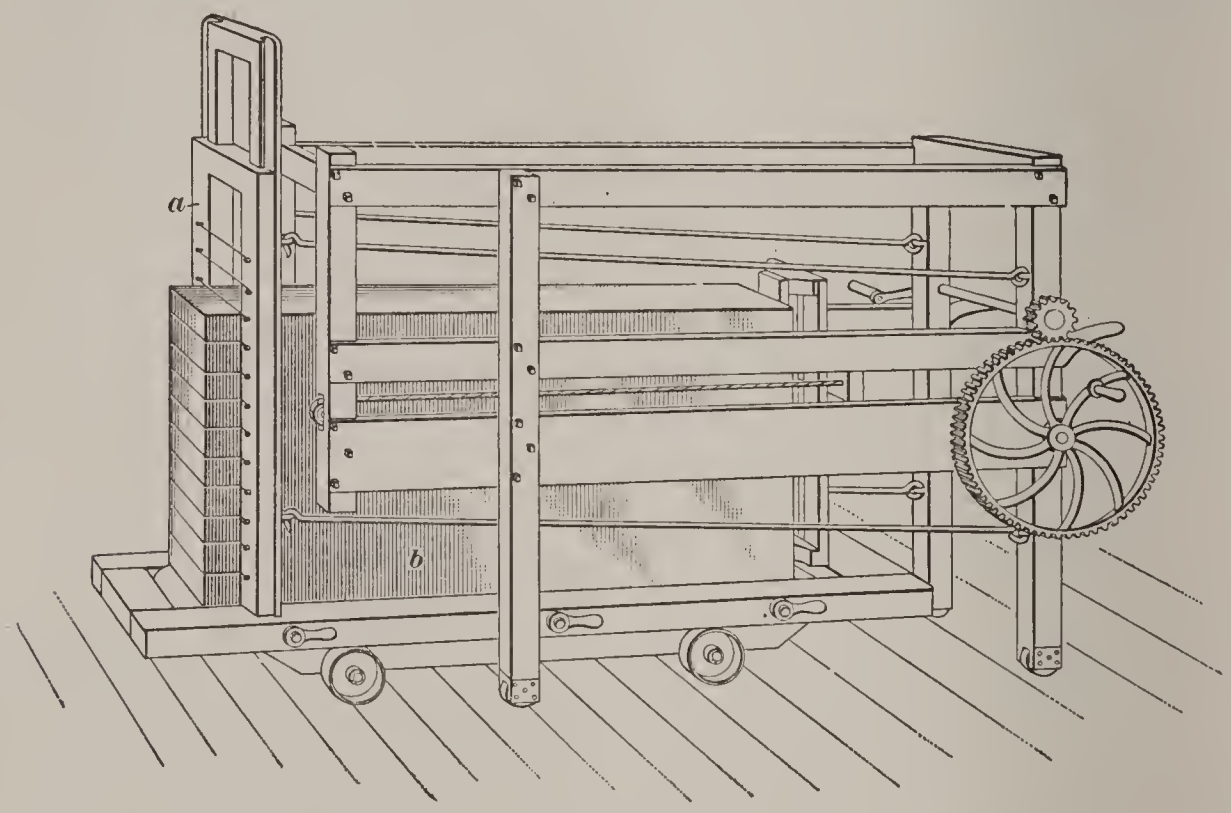


FIG. 16

the slabbed frame out of the cage when the slabber stops automatically.

62. Piano wire is the best for soap cutting. This wire is mounted on the frame head *a,* Fig. 16, in parallel rows at a distance apart corresponding to the width or height of the unpressed bars of soap. The frame of uncut soap is shown at *b.* By means of a key set in the sides of the frame head, the wires may be tightened or loosened as required. With soap that has stood for some time, it is often necessary to remove, for a short distance on both ends of the frame, the layer of soap that has become hardened. This permits the wires to enter the soap easily and to separate from it without the

abruptness that so often injures the wire; it also obviates undue stretching and breakage of the wires.

63. Cutting the Soap.—From the slabber the soap is moved to the cutting table, where it is cut into bars. The fundamental principle of all cutting tables is shown in Fig. 17. A slab is lifted from the pile *a* lying on the frame bottom and is transferred to the table *b*; it is then pushed lengthwise through one or two wires held in the cutting head *c*. In this way, the slab is cut into two or three narrower slabs as wide

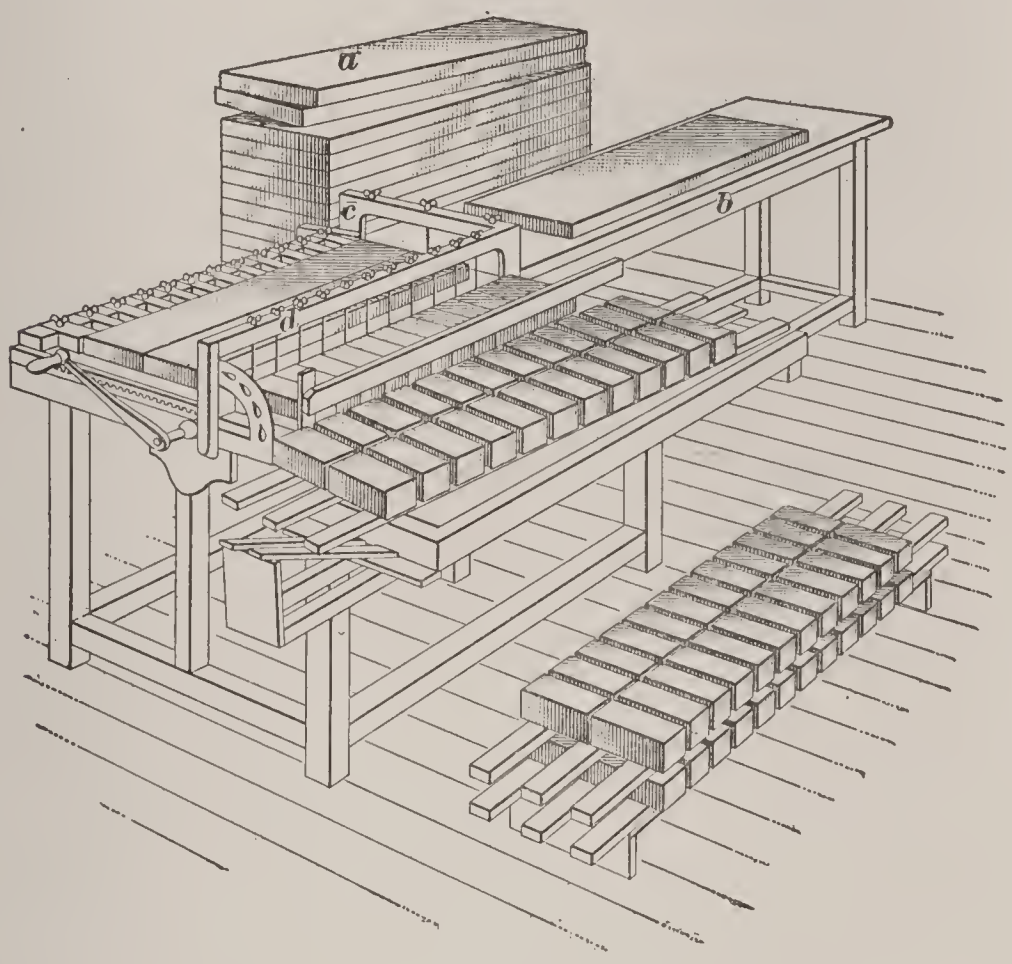


FIG. 17

as the single bar of soap is long. These slabs are then cut at right angles by another attendant to dimensions corresponding to the width and thickness of a single bar. The last cutting movement pushes the slabs through the wires in the cutting head *d*, when, as single bars, they are pushed on a rack supported by an extension of the cutting table. Here, by a slight upward and horizontal motion, the individual bars are separated so that air may circulate between them. The separate racks are placed on a truck until its full quota

has been received. The truck load is then taken into the drying room.

64. The slabbing and cutting of soap are purely mechanical processes and have for their object the division of the frame of soap into bars. The greatest care to be exercised at these stages is to slab and cut the soap to such dimensions that the amount of waste is reduced to a minimum.

Freshly cut soap is soft, sticky, and opaque, and, if properly crutched, should be homogeneous. It contains from 30 to 35 per cent. of water, according to the manner in which the soap was settled and the nature of the additions during crutching. In calculation, it is considered that 100 parts of glyceride soap stock will yield 150 parts of finished soap. The yield is less with rosin alone, and with some stock it may be as great as 157 per cent.

An analysis of pure settled soap at this stage presents the following data:

	Per Cent
Fatty anhydrides	61.80
Combined alkali	7.21
Anhydrous soap	69.01
Water	30.99
Total	100.00

65. Drying the Soap.—Aside from the processes in the kettle, there is no stage in the manufacture of settled soap that requires greater care in its operation than the treatment received in the drying room. While improperly dried soap may cause no great trouble in the press, it is subject to rapid deterioration in appearance, and the influence of this one factor on its ultimate distribution demands that its final treatment in the factory be given the closest attention of the soap manufacturer.

Previous to the introduction of the rapid-drying apparatus, the moisture in the exterior parts of the bar was allowed to evaporate spontaneously. By this method, the drying of soap was an extremely slow and unsatisfactory process, depending

largely on atmospheric conditions. A stove in a closed room was a great improvement. This primitive method, with its manifest disadvantages, was succeeded by a system of hot-air circulation by natural draft. Steam heat by simple radiation from pipes was also employed, and with the introduction of forced draft, the elements of the system of drying in use at present were established.

With laundry soap of good body, sufficient drying before pressing may be obtained in cool weather by standing the rack bottoms full of cut soap in front of an open window. It is necessary with this grade of soap only to get the surface *skinned over* enough so that the subsequent handling does not mar it and also prevents the soap from sticking to the dies of the press. However, in damp weather, and in summer, some artificial drying must be done.

66. Purpose of Drying Room.—The purpose of the drying room is to hasten the evaporation of water from the surface of the bar, so that there may be formed a thin crust of comparatively hard soap. This crust serves to retard further evaporation from the interior of the bar and allows the bar to be pressed and stamped without the soap adhering to the dies. Without the formation of this skin of firm soap, pressing and stamping cannot be done properly.

On cutting a bar of soap into halves, this superficial drying becomes plainly evident. The soap when removed from the drying room and after being pressed has a smooth, glossy, and translucent surface, which condition is in a marked contrast to that observed at the cutting table.

67. During the drying process, from 3 to 5 per cent. of water has been expelled entirely from the surface of the bar, while the interior contains the amount of water originally present, namely, from 30 to 35 per cent. The inequality of moisture contents between the exterior and interior parts of the bar partly explains the sweating to which settled soaps are universally susceptible.

This accumulation of moisture does not develop until after the bar is wrapped and packed. If a freshly pressed bar of

soap without wrapping were allowed to remain exposed to the atmosphere, it would dry, but would not sweat, assuming, of course, that the atmosphere has not attained the dew point. The moisture in the interior of the bar has passed through the hard surface into the atmosphere, and this process will continue until an equilibrium of moisture contents throughout the bar has been attained.

68. With soap wrapped and packed in a box, the conditions are entirely different. The tendency of the moisture to pass from the interior of the bar to the drier surface remains, but further evaporation from the exterior of the bar is checked. Here the moisture accumulates and softens the soap, which in turn adheres to the wrapper. This difficulty is overcome by using a parchment sheet between the soap and the outside wrapper. If the soap contains an excessive quantity of mineral salts, these are carried in an aqueous solution to the surface and on subsequent evaporation of the water form an incrustation. Boxed soap in storage should not be subjected to unnatural fluctuations of temperature.

69. Drying Soap by Forced Ventilation.—The mechanics of the modern soap-drying room represent more the adoption of a similar process employed in other departments of industry than they do a natural evolution from previous efforts in this particular field. The use of centrifugal fans in the production of artificial draft dates from the 16th century, but it was not until Stevens' experiments in the early part of the 19th century that the devices for artificial draft resolved themselves into the systems of ventilation known today, namely, the plenum and the vacuum, or, respectively, the forced and the induced, draft.

In connection with the drying of soap, ventilating fans may be divided into two general classes: the centrifugal fan, or blower, and the propeller, or disk fan. The former is more generally confined to ventilation by forced draft and is designed primarily for removing air under pressure. Fans of the disk type, shown in Figs. 18 and 19, are not adapted to plenum ventilation, where it is desired to move large volumes of air

quickly and under considerable resistance. They find extensive use and are very satisfactory for moving air under slight resistance, as under conditions met with in the ventilation of soap-drying rooms.

70. Both systems of ventilation, the plenum and the vacuum, are used in the drying of soap. The equipment of a drying room under the plenum system comprises, as a rule,

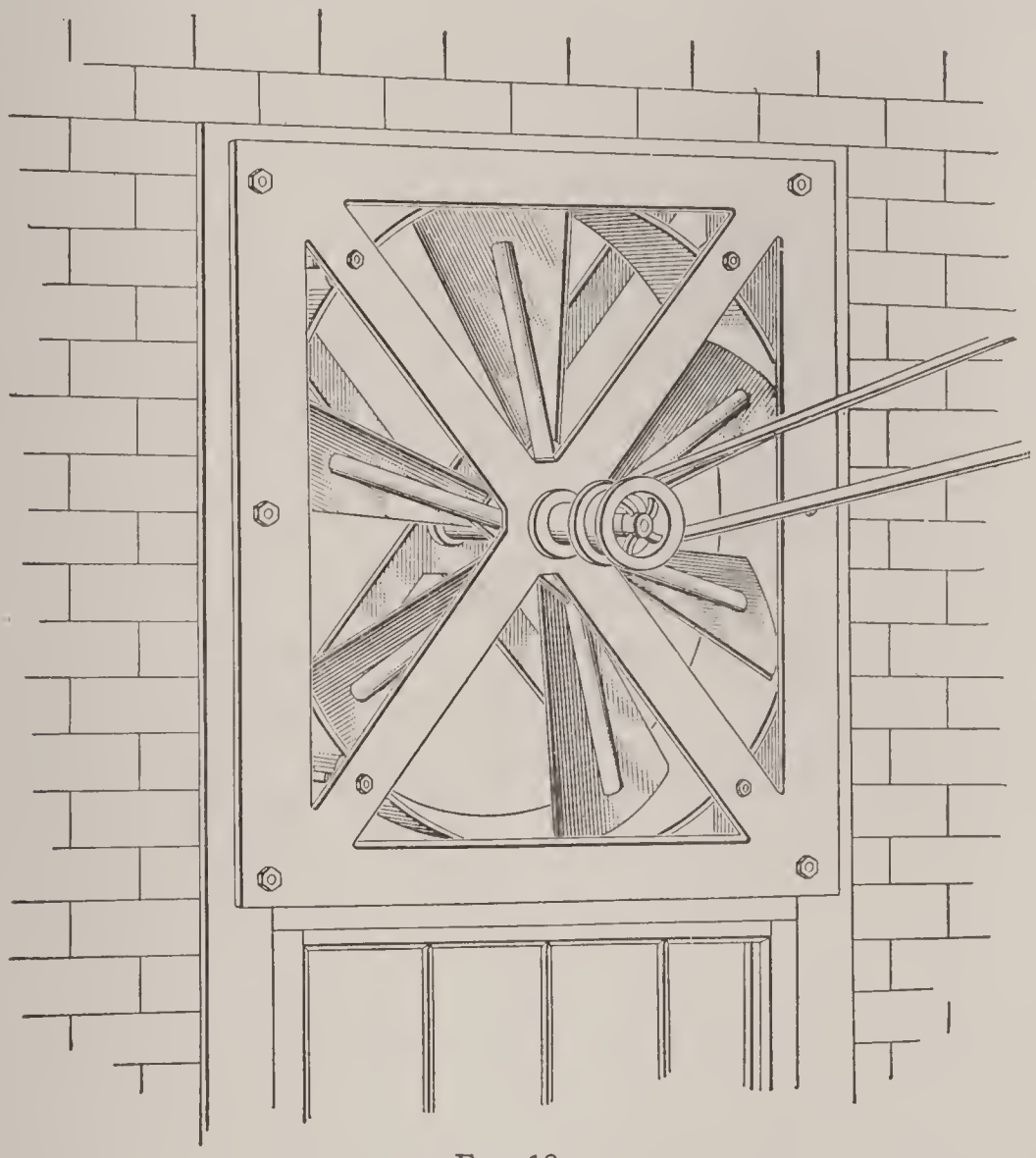


FIG. 18

a disk fan, two arrangements of which are shown in Figs. 18 and 19. In the arrangement shown in Fig. 19, the fan is operated either by a belt from shafting or by a direct- or belt-connected engine or motor and a sectional heater that consists of steam pipes enclosed in a sheet-iron case *a*, communicating with the discharge of the fan case *b*. Air may be forced through the heater and discharged at the desired temperature

into the drying room, or the fan may be interposed and air drawn through the heater and then discharged into the drying room. As the results produced are the same in either case, convenience of application will determine the arrangement.

71. With forced draft, the drying room is best constructed so that heated air enters at one end and leaves at the other, while freshly cut soap is introduced at one side, and, as the drying progresses, is withdrawn at the opposite side. The heater and fan may be placed at opposite ends of the room and the fan used to exhaust the warm and moisture-laden air. This

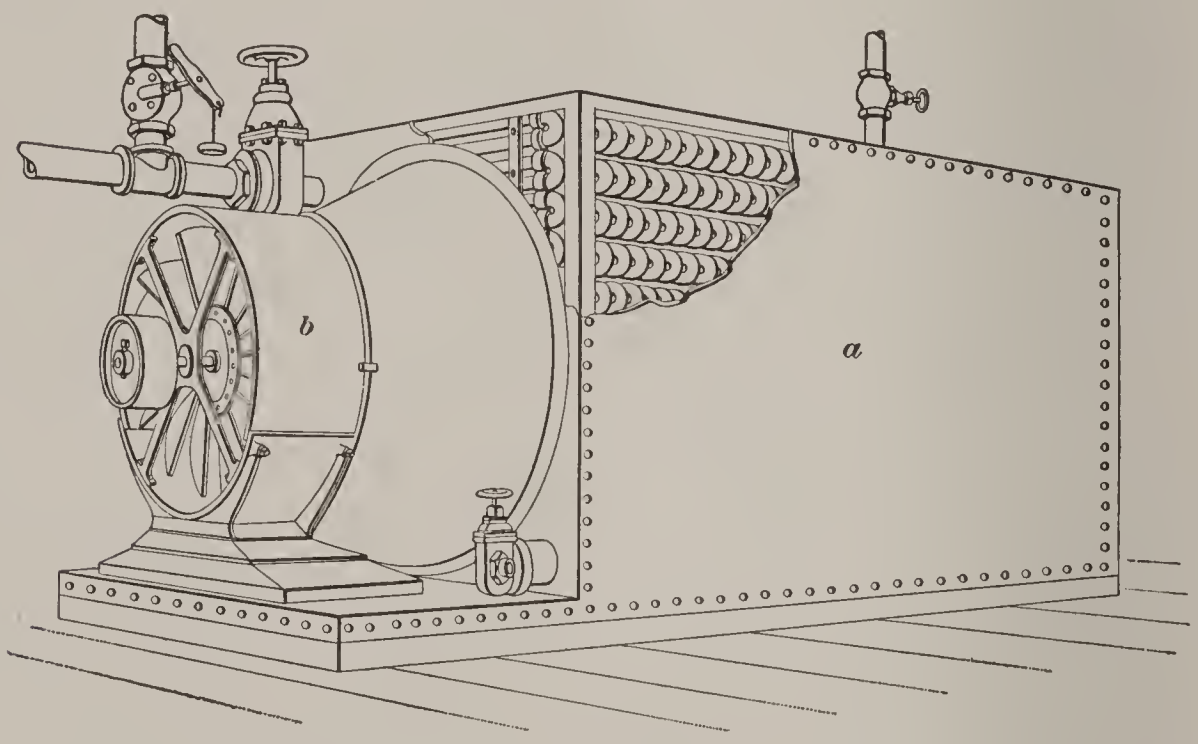


FIG. 19

arrangement presents an example of the vacuum system, or drying by induced draft. The combination of heater and fan shown in Fig. 19 is replaced with advantage by locating the heating coils at one end of the drying room or arranging them in rows throughout the drying room between the trucks of soap. The cheaper and simpler disk fan set in the framework of the wall, as shown in Fig. 18, is, with this arrangement for the drying of soap, equally efficient and satisfactory. The hot-blast drying apparatus shown in Fig. 19, although compact, may occupy valuable space. The exhaust-steam connections with the necessary insulation are simple and easily made.

72. Heating of the Drying Room.—By distributing the pipes of the sectional heater throughout the drying room in rows parallel with the trucks of soap and under openings immediately above for the admission of cold air, not only is a greater uniformity of the drying process obtained, but the use of the cheaper disk fan, which is admirably adapted for ventilation by exhaustion, is permitted. Exhaust-steam connections are made through the floor, and by means of suitably placed valves, exhaust steam may be cut off from any section, thus varying the capacity of the drying room at will.

73. In the drying process, air fulfils two functions: it carries to the moist soap heat necessary for the evaporation of the water and it serves as a vehicle for the removal of the vapor. The capacity of air for heat is very small, its specific heat being only .238, with water as 1; its capacity for vapor depends directly on its temperature and its relation to the dew point, naturally diminishing as the point of saturation is reached. With a rise of temperature, the capacity of air for moisture increases. It is estimated that air at 72° F. has a threefold greater capacity for aqueous vapor than the same volume at 42° F.; at 172° F., its capacity for vapor is more than eighty times as great. Increase of temperature thus means the more rapid formation of vapor, with a much greater increase in the capacity of air for absorbing it.

74. Requirements of the Drying Room.—The essential requirements of the heating and ventilating apparatus of the drying room are that a large volume of air be provided at the required temperature and that this be maintained in rapid circulation. A comparatively low temperature, namely, 90° to 100° F., is productive of the best results. Air maintained at a temperature in excess of 100° F. for a long period causes the soap to undergo an appreciable softening, with more or less discoloration.

The temperature at which soap will melt depends primarily on the nature of the stock and the proportion of water present. In the drying of *green* soap, it is desirable that the currents of warm air circulate lengthwise of the bar, in order that the

largest extent of evaporative surface may be exposed and the drying process thus hastened. The duration of the drying period is easily learned by experience, from the appearance of the bar; it varies from 6 to 12 hours.

75. Pressing of Soap.—Hard soap was originally sold in the United States in bulk. Later, the soap was cut into bars and packed, with the wrappers in bulk, in a box, the retailer himself wrapping the soap as sold. Under present conditions, however, the freshly cut bar is pressed, stamped, and wrapped.

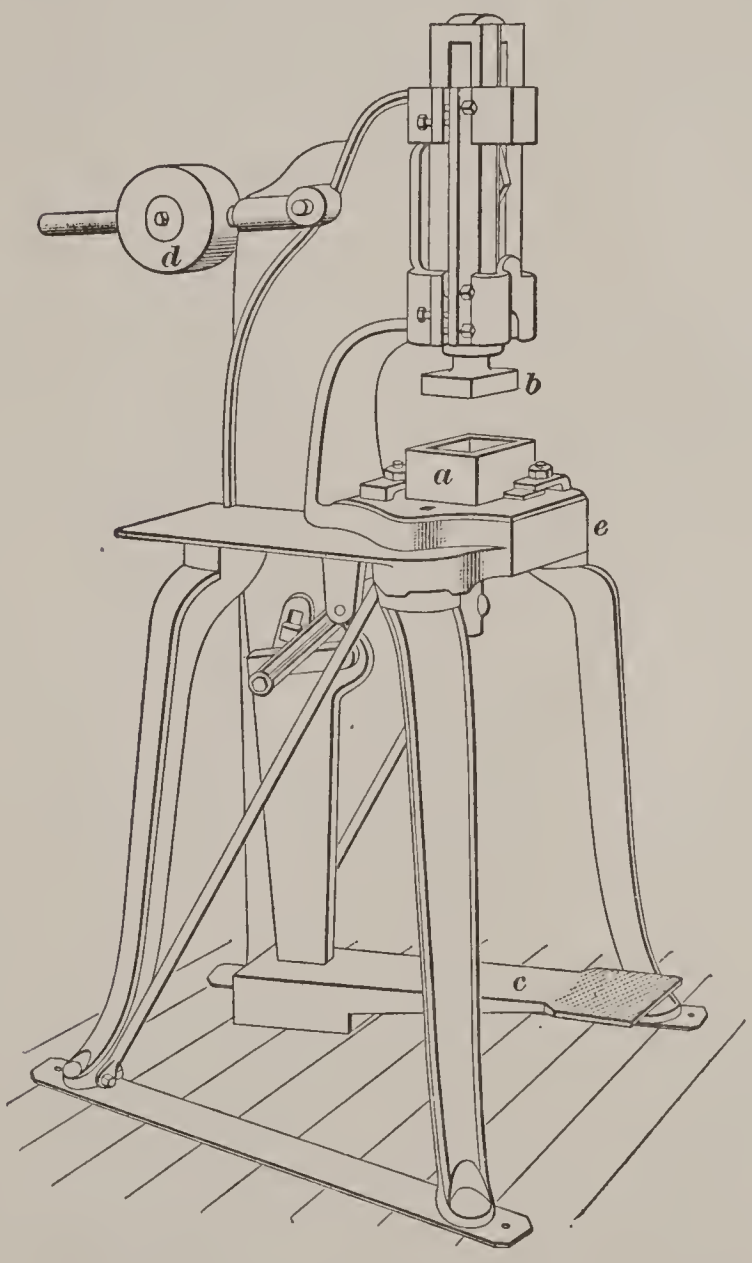


FIG. 20

In Fig. 20 are shown the essential features of a foot-power soap press. This machine is arranged so that the operator can deliver a sudden blow to the cake of soap placed in the die box *a*. The thumb and forefinger of the right hand are used to place the soap in this die box. An operator on a press of this kind will press thirty bars per minute. To prevent soap from adhering to the die *b*, the cake is placed lightly on a bunch of waste saturated with brine or a mixture of vinegar and water that is usually located at the right of the die box *a*. After the blow has been delivered by the right foot placed on the lever *c*, the upper die *b* is lifted by the counterpoise *d*, which also serves

to add momentum to the force of the blow, and a lever action lifts the pressed bar out of the die box *a*. The bar is then transferred, by the left hand of the operator, to a table at his left. The foot-power soap press is built in a number of styles, some being partly operated by steam, as shown in Fig. 21.

76. Steam Foot-Press.—The steam foot-press, Fig. 21, is provided with a steam cylinder *a*, the piston *b* of which is

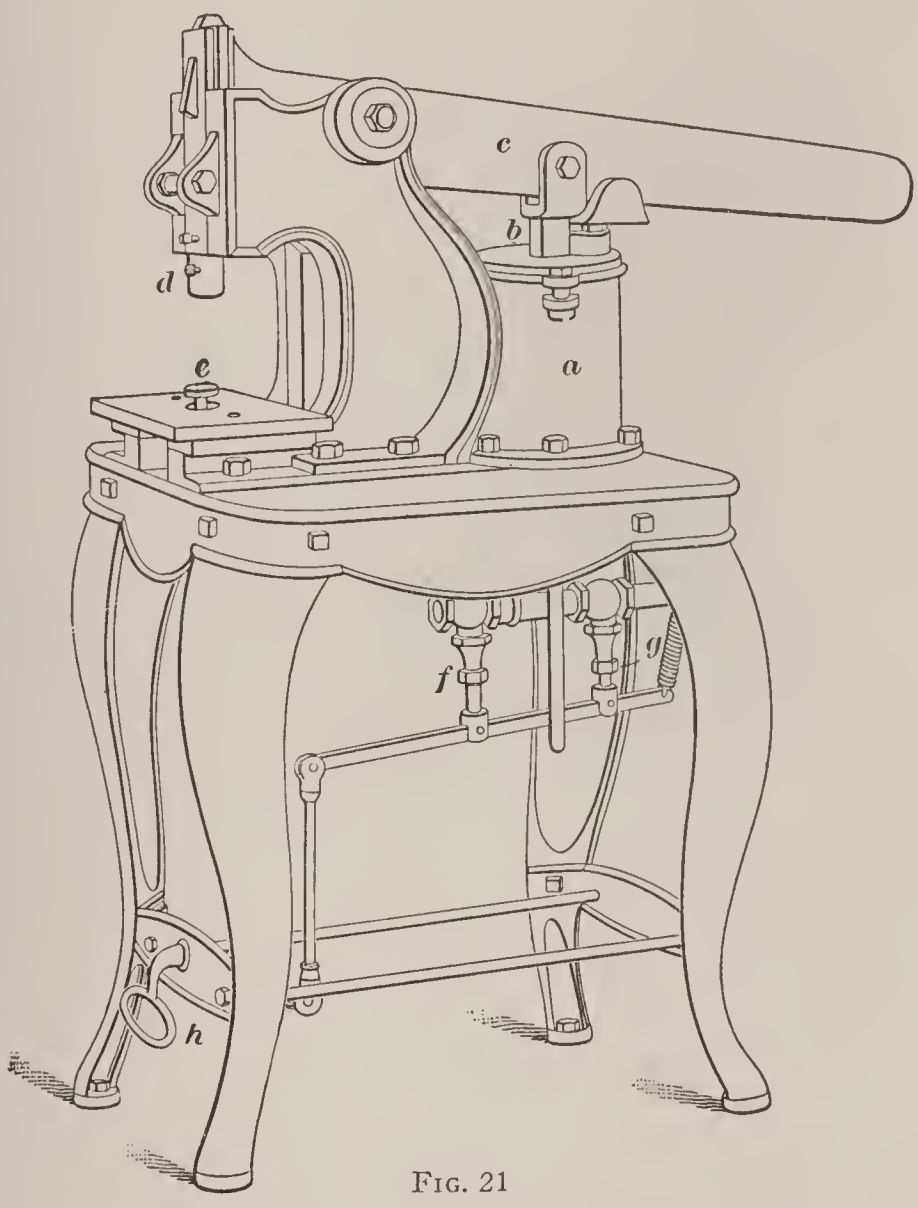


FIG. 21

directly connected with a lever *c* that controls the dies *d* and *e*. A system of valves is arranged at *f* and *g*, from which points, by a slight pressure of the foot on the treadle *h*, steam is admitted to the cylinder *a* and a quick, powerful blow is given to the soap placed over the die box, the lower die *e* of which is elevated as shown. The lever returns instantly, withdrawing the upper die and elevating the lower one, from which the cake

of soap is removed by the left hand of the operator. With rapid work, upwards of 1,500 cakes an hour can be pressed on a machine of this type. This kind of press is not used

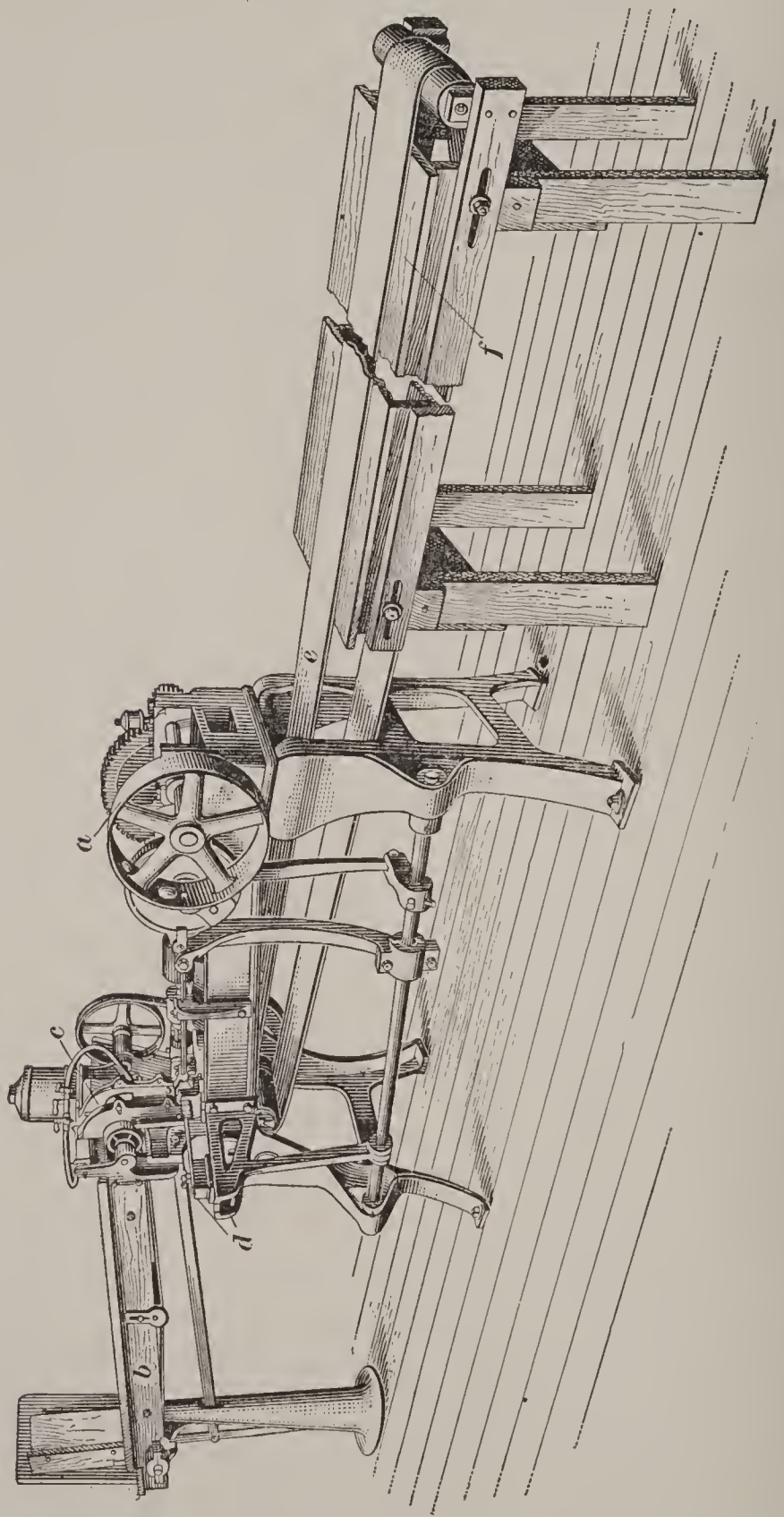


FIG. 22

extensively at the present time; it is replaced by more modern machines, which are entirely automatic and give a much higher output.

77. Automatic Steam-Power Soap Press.—The belt-driven, automatic soap press is a direct development of the old foot-power press, and arose from a demand for greater rapidity of operation. Several styles are on the market, with a guaranteed capacity of from 60,000 to 75,000 cakes per day of 10 hours. They are perfectly automatic in their action, require but little attention, and for a factory producing upwards of 400 boxes of soap per day, such a machine is a safe purchase.

The more improved forms admit of interchangeability of the dies, thus permitting the soap manufacturer to use any die that he may have in stock. Thus all the brands of a single factory can be pressed on the same machine, with no longer time required to change the dies than on the old-style foot-press. On the high-speed presses, a dilute solution of acetic acid (3 to 4 per cent.) is allowed to drip on the dies to prevent sticking.

78. In Fig. 22 is shown one of the latest forms of steam-power soap press. To describe it briefly, power is applied to the pulley *a*, which in turn operates the feeding belt running on the surface of table *b*. This belt carries the cake of soap to the drop box *c*, down which it falls between the two dies impelled in a horizontal plane at *d*. The cake of soap as it falls down the drop box *c* is caught between the two dies, pressed, and dropped on the belt *e*, which carries the pressed bar to the wrapping bench *f*, where it is wrapped and then packed in boxes.

79. In Fig. 23 is shown a three-die rotary soap press. This machine consists of double cylinders *a* and *b* placed end to end, in which rotate cams that automatically bring together and withdraw horizontally two dies that meet in their corresponding die box, of which three are arranged 120° apart. The dried soap from the racks is placed on the feeding belt *e*, from which each bar is singly moved forwards to the die by a *finger* on the chain belt passing over the pulley *d*, to which power is applied at *c*. A set of dies is shown at *f*. The pressed soap is dropped on the belt running in the box *g* and is conveyed to the wrapping bench.

80. Wrapping by hand is done in small establishments. It has been superseded in the larger ones by automatic power machines, the soap coming from the presses feeding directly to

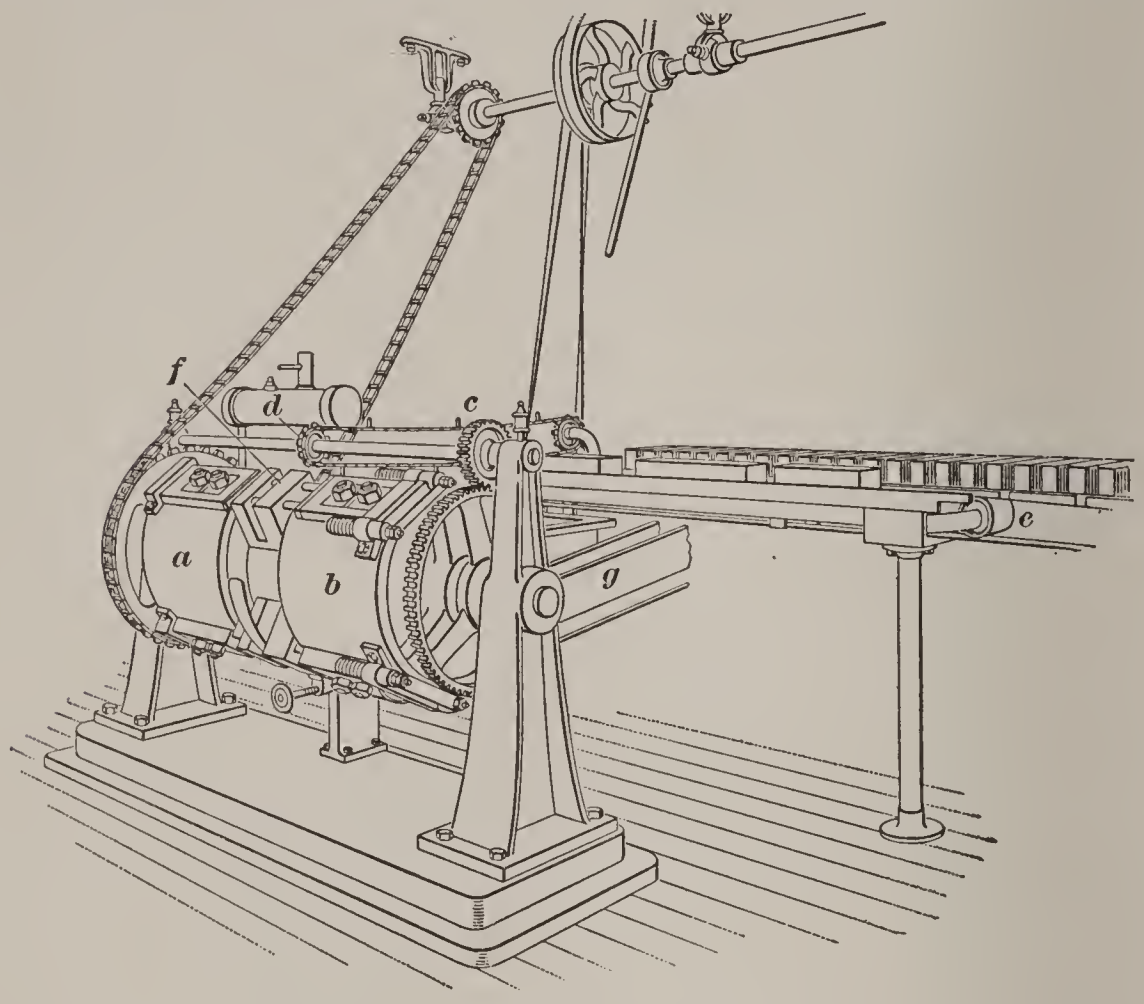


FIG. 23

belts that supply the wrapping machines. The press just described requires two wrapping machines. The wrapped soap is packed into the box as it leaves the machine.

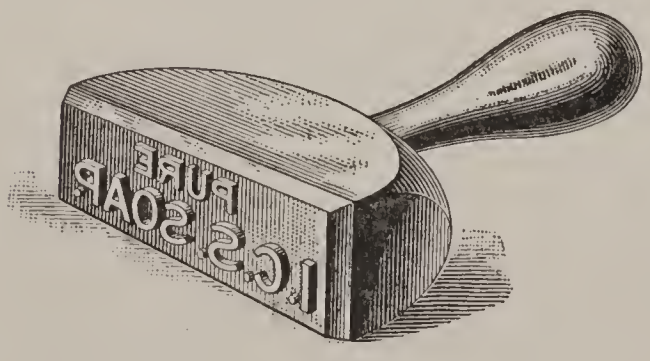


FIG. 24

Among the many advantages possessed by automatic soap presses are chiefly the perfect work, capable, at a maximum speed, of 150 bars per minute; the regulation of the pressure to suit the character of the soap; and the insurance of safety to the operator from loss of fingers. The automatic power press of the capacity stated will do the work of five foot-presses with one-third the labor.

81. Soap Dies.—The kind of die to be used is determined by the kind of soap to be pressed. The function of a die is twofold: it forms the yielding mass of soap into a definite shape and imprints on the cake thus formed, in either elevated or sunken letters, or both, usually the brand of the soap and the name of the manufacturer or vender.

The earliest form is the hand stamp, shown in Fig. 24, by means of which the brand or maker's name is impressed on the freshly cut bar.

82. The second form is the box die shown in Fig. 25. In this form of die, the mold feature is introduced in pressing the soap from above and below in an enclosed space called a *box*. The upper die *a* and the lower die *b* fit closely to the interior of the box *c*. They are so adjusted with the press as to cause their respective downward and upward movement at a separating distance corresponding to the thickness of the pressed bar, which dimension the thickness of the unpressed bar closely approximates. There is thus insured such a distribution of the soap in the mold as to fill every part of it.

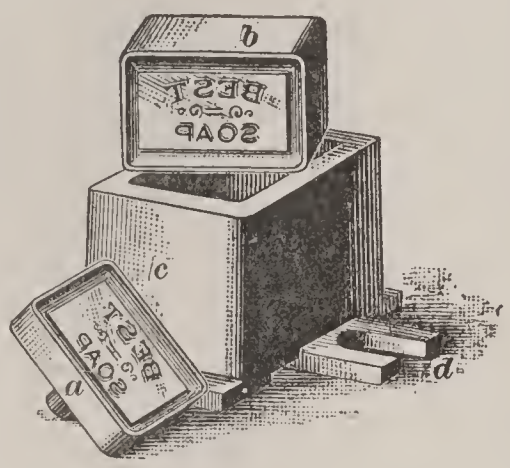


FIG. 25

The same box and dies may be used for different brands, by means of detachable name plates. In fitting the box to the bedplate of the soap press shown at *e*, Fig. 20, by means of the shanks shown at *d*, Fig. 25, care should be taken to insure a perfectly vertical motion of the upper and lower dies; otherwise, they will rub against the interior sides of the box, with the result that the accuracy of the die will soon be destroyed.

83. In the molding and stamping of milled soap, dies of a different construction must be used because of the greater firmness of soap of this character. A powerful and sudden blow must be delivered, and the construction of the die must be such as to expel all surplus soap from the cavity, instead

of, as in the more yielding laundry soap, forcing this surplus into every part of it.

The pin, or shoulder, die is so called from the use of pins and sockets to guide the upper and lower dies, thus preserving

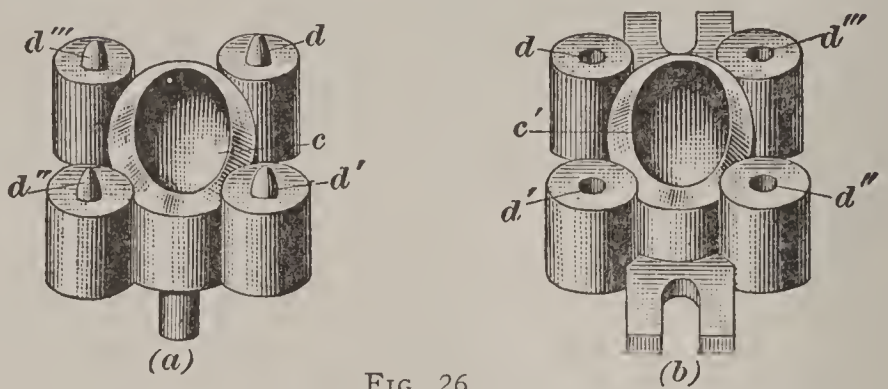


Fig. 26

their accuracy. The term shoulder has reference to the base supporting and receiving the four pegs. As shown in Fig. 26, this third form consists of two dies, (*a*) being the top die and (*b*) the bottom die, without a box, each forming the face and one-half of the cake. The edges *c* and *c'* of the dies strike together, thus forcing out all surplus soap. The guide pins *d*, *d' d''*, and *d'''* of the top die serve to guide it squarely

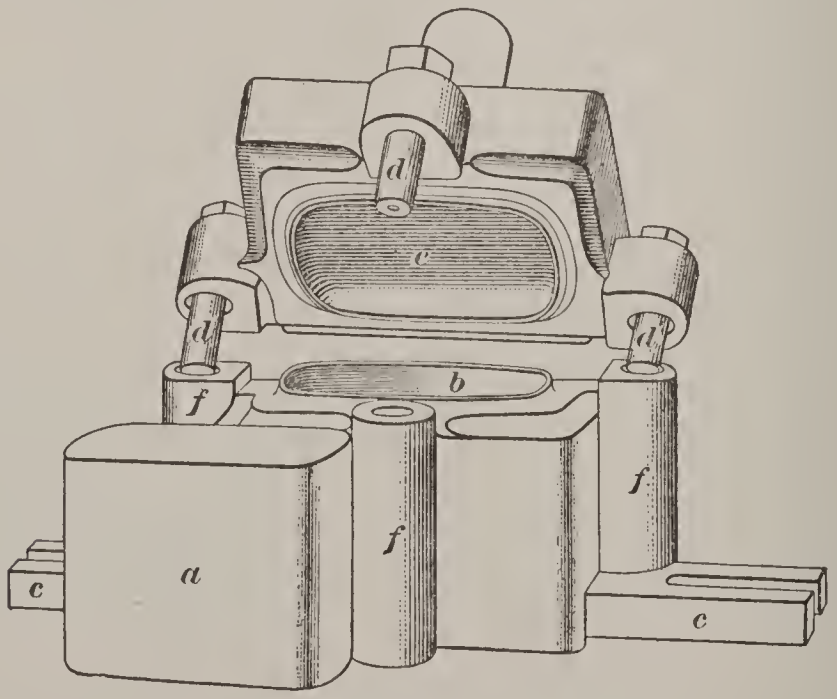


Fig. 27

on the bottom die. The shoulders of the bottom die, receiving the guide pins in the corresponding holes *d*, *d'*, *d''*, and *d'''*, bear the force of the blow, and preserve the cutting edges *c* and *c'*. These dies are also made with removable panels,

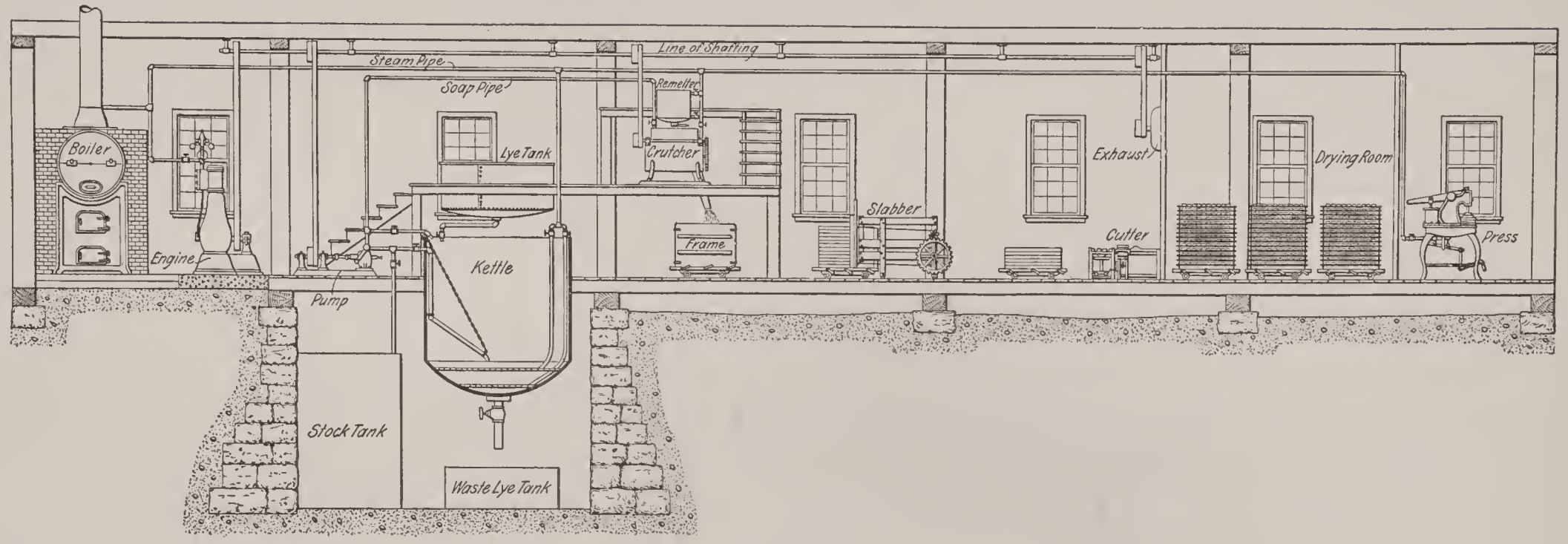

Steam Pipe
Line of Shafting
Soap Pipe
Remelter
Boiler
Lye Tank
Crutcher
Exhaust
Drying Room
Slabber
Frame
Cutter
Press
Engine
Kettle
Pump
Stock Tank
Waste Lye Tank

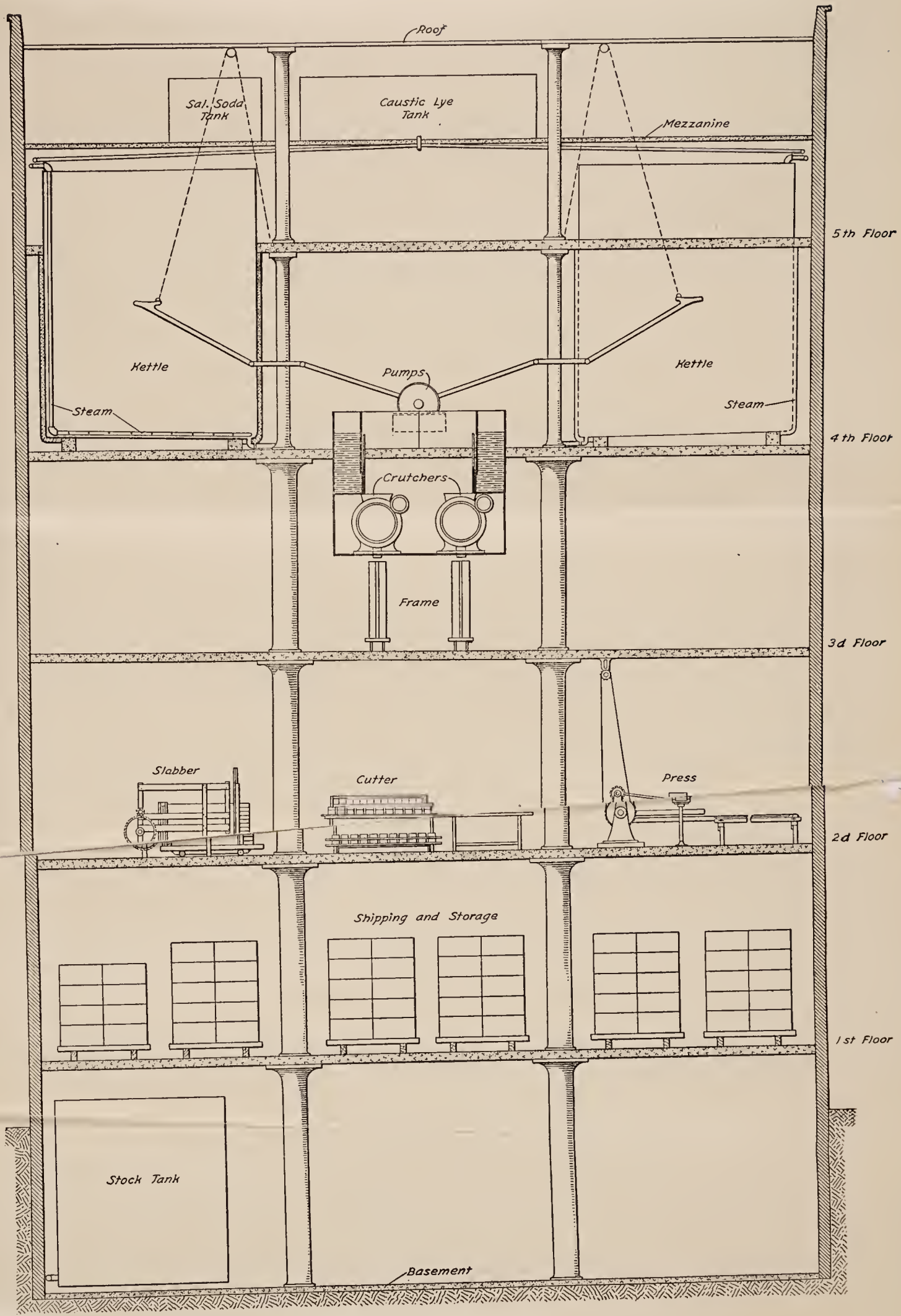
FIG. 28

or name plates, thus permitting a number of brands to be stamped with the same die by inserting a different name plate in the base of the bottom die.

84. The fourth form is a combination of the pin, or shoulder, and box dies, and in addition to possessing the qualities of each, it admits of the pressing of cakes of different thicknesses and weights by virtue of the removable lower die placed in the box. As shown in Fig. 27, *a* is the removable lower die, which is made in varying heights so as to produce a bar of corresponding thickness. It fits into the box *b*, which is fastened by the shanks *c* to the bedplate of the presses shown in Figs. 20 and 21. The guide pins of the top die *e* are shown at *d*, and shoulders of the lower die at *f*.

The dies are made of gun-metal alloy or rolled brass. They should be substantially made with all moving parts carefully fitted. The engraving should be so executed, with letters or figures of uniform bevel, as to produce in the soap clear-cut and even characters, more especially when these are in relief. The workmanship of the die is shown at once in the appearance of the pressed soap. A good die greatly improves the appearance of an inferior product. Toilet soap is stamped on foot-presses, the automatic press having not as yet proved satisfactory for stamping milled soap.

85. Plans of Two Types of Soap Factory.—Two general types of soap factory are shown in Figs. 28 and 29, Fig. 28 showing all the equipment on one floor, and Fig. 29 the gravity plan as used by the larger plants, by which the soap is boiled on the top floor and finished on the way down. From these two plans, in conjunction with the methods and apparatus described in the preceding articles, each operation may be traced.



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SECTION OF 5=STORY BUILDING FOR SOAP MANUFACTURE

FIG. 29

SEMIBOILED SOAPS

86. The term *semiboiled,* as applied to soap, refers to a soap that has not been grained, the saponification being completed in one change and the soap strengthened and settled in the following one. As the soap is not grained, in which process glycerine is separated, the kettle will contain, on the completion of the process, all the material that has been added to it. In semiboiled soap, rosin may be used as an ingredient, but the process is generally used only for straight glyceride stock.

87. As no impurities are removed in the waste lye formed by graining, it is necessary, in order to produce a superior quality of goods, that the stock used be of good grade. This process is often resorted to for the manufacture of the base for cheap toilet soaps. It is used generally for preparing the soap base for soap or washing powders, and is more quickly carried out than is the manufacture of settled soap. The stock can be killed (saponified) in the early forenoon, strengthened in the afternoon, and pumped to the crutcher, if a filled soap or a soap powder is to be made, or directly into the frame, if intended for toilet soap, on the following morning. If it is desired to save the glycerine and to remove the impurities as well, the soap may be grained sharply after the stock has been killed, the waste lye withdrawn on the following morning, and the soap carefully strengthened, settled, and pumped from the kettle on the third day.

88. The semiboiled process is primarily a cheap method of soap manufacture, with economy in fuel, labor, and time. The best plan, however, is to give the soap a simple purification by graining it sharply, thus prolonging the time consumed in manufacture by one day. If this is done, the grained soap should stand overnight before drawing the lye. By doing so, the volume and depth of color of the niger is greatly reduced.

The semiboiled process is used as well for the manufacture of soft soaps, of which textile soap is a variety, and for green

Castile soap made from olive-oil foots. A desired characteristic of the latter soap is the green color arising from the green coloring matter, or chlorophyl, present in the rind and pulp of the fresh olive. This soap is never grained. In graining, the coloring matter would be discharged into the waste lye, with the result that the finished soap would bleach rapidly and unequally on exposure, thus detracting from its appearance.

89. Manufacture of Soft Soap.—As the semiboiled process is used for the manufacture of soft soap, the boiling of this quality of soap will be discussed in outlining the practical features of the process.

Straight tallow or good grease stock, to which may be added some cottonseed oil, is run into the kettle on open steam. According to Table XIII, *Manufacture of Soap,* Part 1, for saponifying 10,000 pounds of tallow with caustic-soda lye of a density of 20° Baumé, made from 74 per cent. caustic, 9,795 pounds will be required. As tallow is a stock that is easily killed and gives well-defined indications of conditions in the kettle, practically all this lye may be added by the time the stock is in. Saponification, however, progresses in the meantime. The chief care is to avoid bunching, by boiling the contents of the kettle vigorously. Open steam is used throughout the process.

90. In the manufacture of settled rosin soap, a hard soap was produced; in the present case, however, it is desired to turn out a soft soap made with a soda base. According to an old definition, a soft soap is one in which the alkali used is potash. That definition is obsolete, for the hardness of a soap does not depend primarily on the nature of the alkali present, but on the degree of hydration of the soap. A hard soap can be made of potash and olein, which were the ingredients of the original Castile soap.

With settled hard soap, a yield of 150 per cent. is generally obtained; with soft soap, a yield may be obtained varying from 225 to 240 per cent. In fact, the yield may be any amount up to 400 per cent., according to the purpose for which the soap is intended.

91. After the stock has been thoroughly killed, the soap is opened slightly with caustic and boiled. This treatment is equivalent to a strengthening change without the intermediate graining. After having boiled quietly on this strength for some time, with an occasional addition of caustic lye as it has been absorbed, add water gradually until the soap closes. There is now in the kettle the soap-maker's 150 per cent. yield, and the soap is in a condition similar to that of settled soap on the settling change. The degree of hydration is determined either by the specifications of the purchaser or by the price obtained for the product. After the soap has been closed, water is added slowly, care being taken to boil it through the mass thoroughly after each addition, until the soap has been brought to that consistency determined by experience.

92. A more satisfactory method, and one depending less on the variable and confusing conditions in the soap kettle, is to add the regulated amount of water to the soap in the crutcher. After thoroughly incorporating the addition in the crutcher, the soap is dropped into tight, weighed barrels and allowed to cool. The barrels are then headed and weighed. There is no market in the United States for package-made soft soap; it is sold in bulk to institutions for cleansing purposes, and in greater quantities to textile manufacturers.

93. When the soap is hydrated in the kettle, the yield is variable, owing to the difficulty of determining the loss of water by evaporation, and in successive boils it may vary several per cent. In the manufacture of soft soap with unmixed stock, as tallow alone, there is not sufficient difference in the amounts of the various glycerides present to produce the *figging* so often desired in a soap of this character. With soft soap made from cottonseed oil, with a small proportion of tallow, the *figged* appearance on cooling may easily be obtained by virtue of the different solidifying points of soaps made from glycerides of different melting points.

94. Soft soap made from caustic potash will admit of a higher yield within the limits of the quality of the product

desired. This arises from the greater combining weight of caustic potash, the molecular weight of caustic potash being 56, while that of caustic soda is 40; also from the fact that a potash soap in a hydrated condition will stand a greater amount of saline filling than will a soda soft soap.

Rosin is used to a great extent in soft soaps, but it should never be present in textile soaps. Linseed oil is extensively used in European practice, and, in fact, may be said to be the chief ingredient. Soft soaps admit of adulteration to a high degree, the principal cheapeners and adulterants being aqueous solutions of sodium silicate, soda ash, and potassium chloride; starch is also largely used.

95. Calculation of Yield.—To ascertain the net percentage of yield, simply divide the net weight of soap made by the weight of soap stock used. To arrive at the total yield, the numerator is increased by the weight of the filling material added to the soap in the crutcher or in the kettle.

COLD-PROCESS SOAP

96. In the discussion of the settled and semiboiled processes of soap manufacture, it was learned that the latter is the more economical, and for the manufacture of soaps of a certain character, it is the preferable one. The ease with which the soap can be purified by graining and removing the waste lye containing the impurities, indicates the looseness of the line of demarcation between the two processes. In the discussion of the manufacture of soap by the cold process, a method that surpasses all others in the economy of every element entering into the cost of production, is introduced. The method, however, possesses certain paramount disadvantages, which restrict its use to a very limited field, notwithstanding the large amount of soap of this character that is produced. The mechanical equipment required consists simply of tanks containing the fat, oil, and caustic-soda lye; a crutcher in which the ingredients are mixed; and frames to receive the mixture and in which, under favorable

conditions, the chemical reaction of saponification continues to completion.

With such simple and comparatively inexpensive factory equipment, it will be evident that the proportion of fixed charges in the cost of the product is very small. Experience is the chief and most important asset, without which, notwithstanding the simplicity of the process, satisfactory results cannot be assured.

97. The term *cold process* is loosely descriptive. The saponification is not conducted in the cold, for the heat generated by chemical combination is considerable. The term has reference chiefly to the fact that heat is not employed as in the two general processes previously described, only enough heat being used to insure the liquid condition of all the ingredients.

The theory of the process is very simple. The essential requirements are that the ingredients taking part in the reaction be intimately mixed. To effect this, the fat or oil must be in a liquid state and the caustic-alkali solutions must be maintained at such a temperature that when the stock and alkali are mixed, neither will cool the other to stiffness before every particle of the glyceride is brought into contact with the alkali. Even in the daily working of the process, it is a very difficult matter to maintain uniform conditions and to insure the complete absorption of the alkali. As the process is ordinarily practical, saponification is invariably incomplete, with more or less free fat and free alkali remaining in the finished product. This is the chief disadvantage of the process, and is the one that greatly restricts the use of cold-process soap for toilet purposes.

98. To secure satisfactory results in the practical working of the process, it is necessary that the caustic alkali be of high grade, not of lower quality than 76 per cent., and that the glyceride stock be fresh and pure. Without these primary qualifications, good results under no circumstances can be assured; but with them, the prime essentials of satisfactory work are obtained.

Coconut oil, either alone or in admixture with tallow and cottonseed oil, is chiefly used for cold-process soap. The rapid absorption of alkali at a comparatively low temperature, with the production of a smooth, clear soap that will neither crack nor warp on aging and that will admit the incorporation of a large amount of filling, make this oil especially adapted as a raw material for soap of this character. With inferior grades of coconut oil, boiling on strong caustic of 36° Baumé with open steam will remove what free fatty acids there are present, and these, with the impurities, will easily settle out. The same preliminary purification is also required for tallow.

The manufacture of cold-process soap received great impetus from the manufacture of high-grade caustic soda; the impurities always present in low-grade caustic interfered greatly with the satisfactory working of the process.

99. Manufacture of Cold-Process Soap.—To explain the process in practical detail, the manufacture of cold-process soap from 500 pounds of coconut oil will be discussed. By referring to Table XII, *Manufacture of Soap,* Part 1, it will be found that coconut oil will absorb about 17.6 per cent. of chemically pure caustic soda. This amount is equivalent to 18 per cent. of 76 per cent. commercial caustic; therefore, 90 pounds of caustic soda of this grade will be required for saponification.

A caustic-soda lye of 35° Baumé, made from 76 per cent. caustic, contains 28.28 per cent. of sodium hydroxide. Therefore, to furnish 90 pounds of sodium hydroxide, 318 pounds of 35° Baumé caustic lye, made from 76 per cent. caustic, will be required

100. The purified coconut oil at a temperature of 115° to 120° F. is run into the crutcher, and the latter is then agitated. The required amount of lye is then run in, and crutching is continued until a portion of the mass removed on a paddle appears clear and homogeneous. This condition can be ascertained only by experience, and under no consideration should the contents be removed from the crutcher until the most thorough mixing possible has been effected. The mixing

period need not exceed from 20 to 30 minutes, and with experience the time required is usually less. The mass is then dropped into frames, which are removed and carefully covered with soda-ash bags or other suitable material so as to prevent too rapid cooling. The frames should not be exposed to currents of cold air nor in any way subjected to rapid cooling.

101. There were added in the crutcher 500 pounds of coconut oil and 90 pounds of solid caustic dissolved in 228 pounds of water. This mixture yields a soap that, in so far as hydration is concerned, corresponds to the composition of unfilled settled soap. A yield of practically 63 per cent. has been obtained. By adding tallow and cottonseed oil in suitable proportions, the cost of the soap may be greatly reduced; also, the yield may be increased and the cost greatly reduced by the addition of sodium silicate, soda ash, pearl ash, mineral soap stock, starch, or talc.

102. All the filling material in cold-process soaps is generally mixed with the lye previous to being added in the crutcher. If it is desired to perfume the soap, the essential oil is added directly to the mass in the crutcher toward the end of the mixing process.

It should be borne in mind that the more highly filled a cold-process soap is, the more is the process of saponification retarded through the presence of inert material. Cold-process soap will admit of more filling than will settled soap without a corresponding deterioration of appearance on aging.

The substitution of caustic potash for a portion of the caustic soda is desirable, as a clearer, smoother, and milder soap will result.

103. In the procedure just described, there has been no interference on the part of the attendant. The ingredients were mixed in the calculated proportions, and the mixture thus obtained was treated mechanically in the hope that the results would be satisfactory. As experience in the operation of the process is acquired, the treatment may be modified

according to the judgment of the attendant. In the following procedure the judgment of the manufacturer is called into play.

Add the coconut oil at a temperature of 115° F. to the crutcher and start it slowly; then add gradually the caustic-soda lye, which was prepared at the same temperature. When all the caustic-soda lye has been added, continue crutching at the same or only slightly greater speed for a period of 5 minutes. At the expiration of this period, stop the crutcher and enclose it with a cover and soda-ash bags so as to retain the heat. Allow the mass to stand for an hour and then start the crutcher slowly. If a simple mixer

TABLE VI

FORMULAS USED IN MAKING COLD-PROCESS SOAP

Ingredients	Formula No. 1 Pounds	Formula No. 2 Pounds
Tallow	75	75
Coconut oil (Ceylon)	25	25
Caustic-soda lye (35½° Baumé) made from 75 per cent. caustic	75	70
Silicate of soda, N grade . .	125	100
Pearlash lye, 36° Baumé . .	20	17
Amount of soap produced . .	320	287

of style A, Fig. 6, is used, the contents should not rise above the level of the topmost horizontal arm; if it does, this portion of the contents will not be thoroughly mixed. With a crutcher of style B, Fig. 7, the contents should not rise above the level of the central cylinder enclosing the screw. With a steam-jacketed crutcher, the process can be more easily controlled through the use of steam, should the temperature fall below that ascertained by experience to be best, namely, 160° F. If at this stage the soap should show an excessive sharpness to the tongue, a few pounds of coconut oil may be added and crutched in until the soap tastes free

from caustic. On the contrary, should the soap, after the maximum heat of the reaction has been evolved, be neutral to the taste, a few pounds of 15° Baumé caustic-soda lye may be added and thoroughly incorporated. After these adverse symptoms have been corrected, start the crutcher at full speed and continue crutching for fully 20 minutes, until the mass rises white and smooth to the top of the crutcher. The perfume is now crutched in and the soap framed.

104. Manufacture of Cold-Process Soap Directly in the Soap Frame.—It is possible to make a fairly satisfactory cold-process soap directly in the soap frame, thereby eliminating the crutcher. Elkington has given instructions for the manufacture of cold-process soap by this method according to the formulas given in Table VI.

105. Weigh out the proportions of tallow and coconut oil required for a frame of soap into a tight frame. Weigh out the quantity of caustic-soda lye required into a separate vessel; also weigh out the proportion of silicate of soda needed into another vessel. The pearlash (crude potassium carbonate) solution is then weighed out and mixed with the silicate of soda. When all is ready for mixing, the temperature of the tallow and coconut oil in the frame should be from 145° to 150° F. in cold weather and from 125° to 130° F. in warm weather. The caustic-soda lye, and silicate of soda mixture should be at the normal temperature of the factory.

When the temperature conditions are as just stated, the caustic-soda lye is run alone and quickly into the frame containing the mixed tallow and coconut oil, the mass in the meantime being crutched vigorously from the bottom of the frame. After adding the caustic-soda lye, crutching should be continued until the mass begins to thicken. The mixture of sodium silicate and pearlash lye is now added quickly, with continued crutching.

106. After the last addition, the mass in the frame will be thinned out considerably and with continued crutching will gradually acquire a thick, creamy consistency. The two hand

crutches are now removed, and the frame is carefully covered and allowed to stand without disturbance until the soap is cold. If the soap is to be perfumed, the essential oil is stirred in with the silicate of soda mixture and added with it. If the frame must be moved from where the soap is made, move it quickly before the silicate of soda mixture is added; then add this mixture at once and finish the soap as directed. The cold process is primarily a quick process, the tardy addition of any ingredient being sufficient to mar the results.

107. For a 1,000-pound frame, the caustic-soda lye must be run into the soap stock in from 90 to 120 seconds. The addition of the silicate of soda mixture should also not require more time than this. Two crutches (see Fig. 15) should be used, the work carried on quickly, and the bottom of the frame reached at each stroke. With satisfactory conditions of temperature, the time required in preparing a frame of cold-process soap as just outlined should not exceed from 12 to 16 minutes. Care should be taken not to crutch the mass too long. To insure a smooth soap, crutching should be stopped as soon as a mark made on the surface of the soap will remain, and under no circumstances should the frame be disturbed until the contents is cold. With good, firm tallow, cottonseed oil may be substituted for it to the extent of 30 to 50 per cent., and less if the tallow is softer. With soft stock, more time will be required for cooling.

108. The apparatus used in cold-soap manufacture admits of very convenient arrangement. The soap-stock and alkali tanks should be placed on an elevation above the crutcher and should be provided with closed steam coils for heating the contents to the required temperatures.

Successful operation can only be carried out by weighing the stock and the alkali. If two scales are available, tanks sufficiently large to hold stock for five frames may be used, the weight each time being taken by difference. The stock and alkali are run from the storage tanks to the weighing tanks, and from there to the crutcher. If only one scale is available, the tank need be only large enough to charge one

frame, the stock being weighed out and emptied into the crutcher, and after this the alkali and filler, if any is used. In this manner, mistakes in the weights of the material used may be avoided.

109. In summing up the advantages and disadvantages of the cold process, it may be stated that the soap is simply, easily, and quickly made, with but little outlay for plant and labor. It admits of a greater yield than that furnished by any other process for the manufacture of hard soap. A well-made cold-process soap has not only a better appearance than a boiled soap, but retains its good appearance longer. It admits of a greater degree of filling than does a settled soap. The process differs greatly from the boiled processes in one important particular, namely, that small quantities can be made at a time. The process is used extensively for cheap toilet soaps, in few instances for laundry soap, and almost entirely in the manufacture of chipped soap that is sold to laundries.

As ordinarily practiced, the process does not admit of complete saponification, as do the boiled processes, the soap invariably containing, according to the care and experience used in its manufacture, greater or smaller amounts of free caustic alkali and uncombined fat or oil. Rancidity soon develops from the presence of uncombined oil. This is the chief, and practically the only, disadvantage of the cold process.

MANUFACTURE OF SOAP

Serial 2055C (PART 3) Edition 1

REMELTING OF SOAP

1. Purpose of Remelting.—Soap scraps result from various sources, which may be enumerated in the order of their occurrence, namely, frames of soap that have cracked or fissured or for any cause are not suitable, either in whole or in part, for slabbing and cutting; scrapings from frame bottoms; defective bars and trimmings from the cutting table; spoiled bars from the soap press; and unsatisfactory boxed soap returned by the trade. Such soap contains its proportion of the filling added in the crutcher, and if the soap were returned directly to the soap kettle, this filling would be lost in the waste lye. The function of the remelter is to remelt these scraps, and when melted, the soap is crutched and framed as before. Whenever possible, it is more economical to use up the clean scrap in the crutchers. The small amount that cannot be utilized in this manner may be boiled over again.

2. Some perfume and usually a small quantity of soda-ash solution are generally added to the remelted soap in the crutcher. The texture of remelted soap, when cut and pressed, differs from that of freshly pressed soap in being less clear.

When possible, it is always best to place the remelter above the crutchers and not to crutch the remelted soap alone, but to mix it with fresh soap coming from the kettle. The amount of soap, or scrap, to be remelted is usually equal to about 10 per cent. of the output of the factory, so that if

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frames having a capacity of 1,200 pounds are used, each crutcher should have 120 pounds of remelted soap added to it. By following this method, a uniform product is possible—one feature of the soap trade that is very essential in order to insure a successful and profitable business.

3. Remelters.—As shown in Fig. 1, a remelter consists of a sheet-steel tank with a system of closed steam pipes *b* arranged vertically inside and also a system of closed

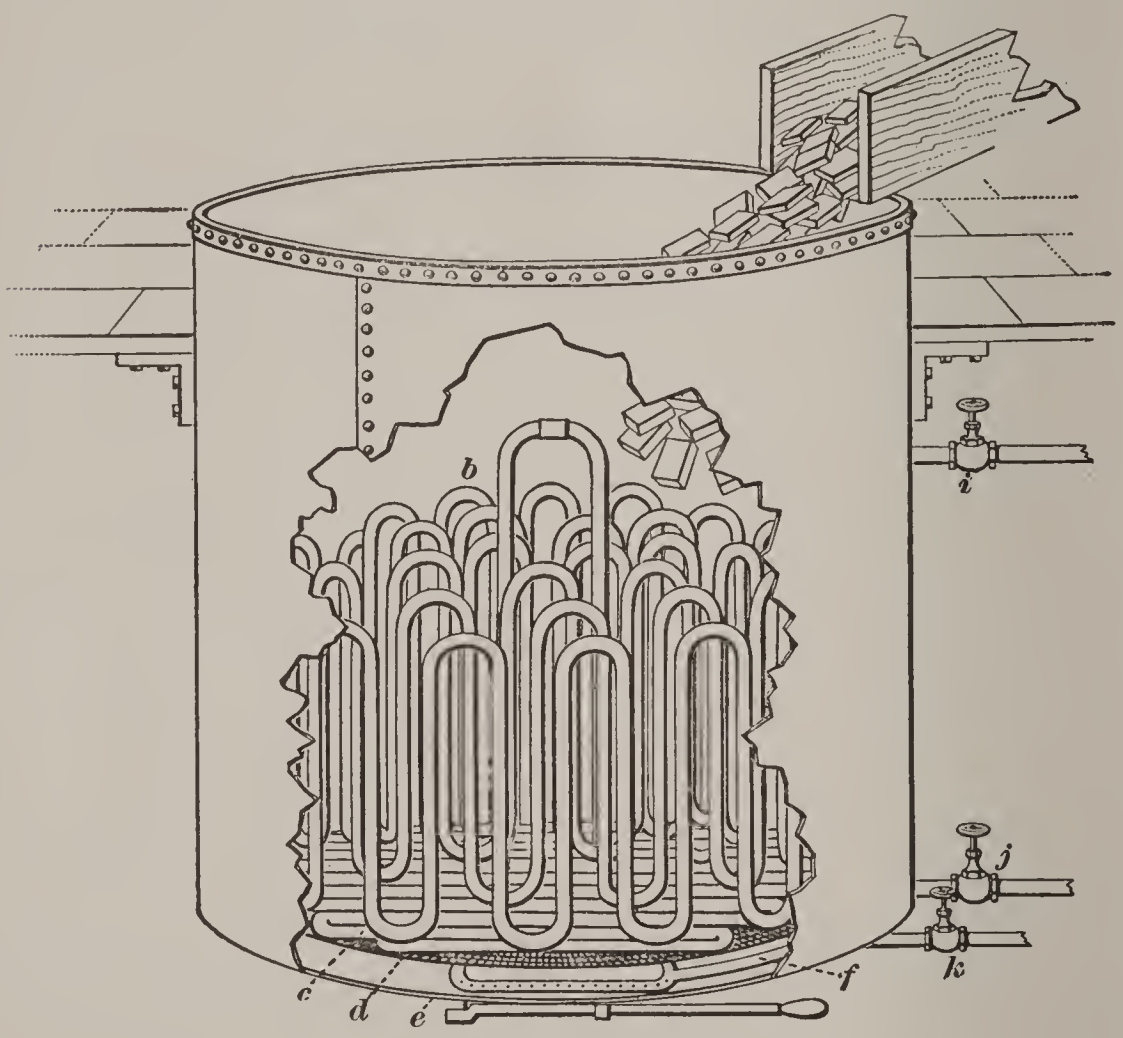

FIG. 1

steam pipes *c* arranged horizontally on the bottom and a short distance above the outlet *e*, the pipes *c* being connected with pipes *b*. A coarse wire netting *d* serves as a strainer; it is placed below the steam coils *c* and above the open steam jet *f*. The pipe *i* carries steam to the upright system *b*; the exhaust pipe *j* carries the water of condensation from the horizontal system *c*; and the live-steam pipe *k* supplies the steam jet *f*. The remelter is usually covered with insulat-

ing material, to retain the heat, and is surmounted by a wooden casing so as to receive the soap on the floor above. The steam pipes are so arranged as to distribute the heat uniformly throughout the mass and to interfere least with the flow of the melted soap, by gravity, from the bottom of the remelter.

4. When sufficient scrap for several frames has accumulated in the remelter, steam is admitted into the closed coils and the adjacent soap is melted. Live steam is then

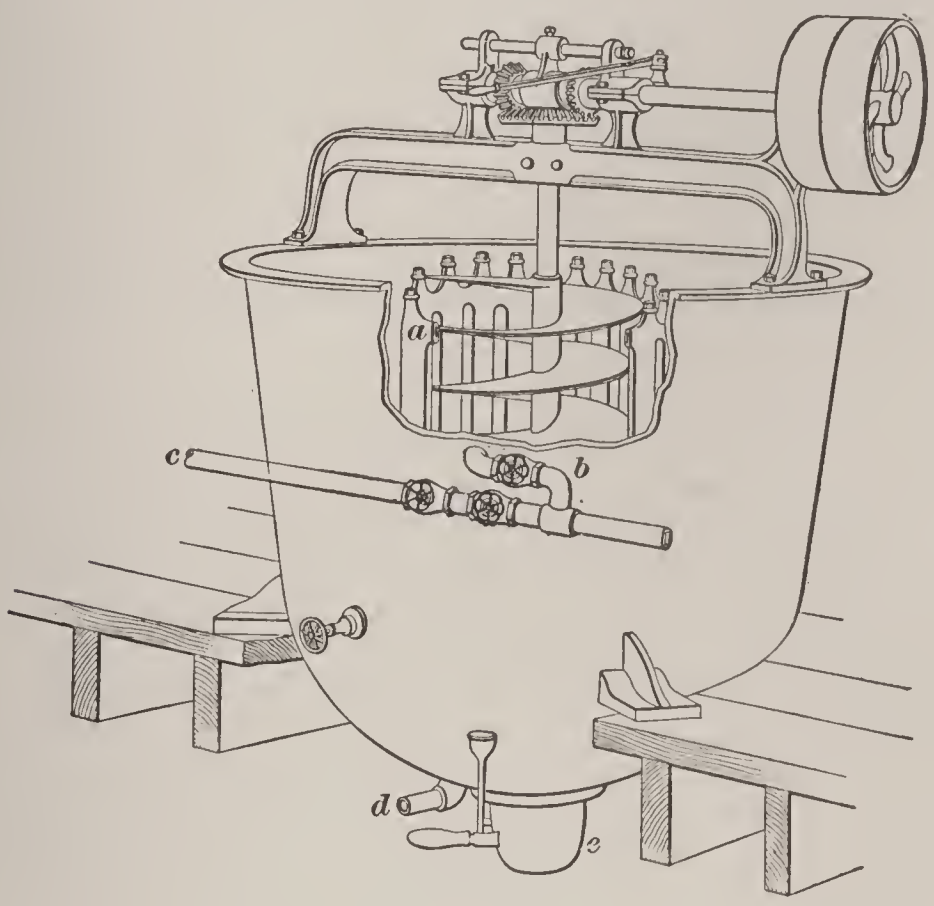

FIG. 2

introduced for a period of 10 minutes in addition to the closed steam. At the expiration of this period, the remelted soap should flow freely from the outlet. The live steam is now turned off. When a sufficient mass has melted to charge the crutcher, which is usually placed below the remelter in factories where a separate remelter is used, framing is begun and continued as fast as the soap melts. The remelted soap withdrawn is replaced by unmelted soap, which sinks by gravity from the wooden casing surmounting the remelting tank.

5. Remelting Crutcher.—When the size of the factory does not warrant the installation of a separate remelter, the latter may be combined with the crutcher, as shown in Fig. 2. The remelting crutcher, as this device is called, is a crutcher in which the inner concentric cylinder is replaced by vertical, closed steam pipes surrounding the screw. Steam is admitted into the vertical, closed steam pipes *a* through the valve *b*. Live steam is introduced at *c*, and the water of condensation is withdrawn from the closed steam pipes at *d*. The outlet of the crutcher is at *e*. The remelting of soap in this device is carried on practically the same as with the regular remelter. Soap scrap may be introduced by gravity from a receptacle placed above the crutcher.

MANUFACTURE OF TOILET SOAP

MILLED-PROCESS SOAP

6. The manufacture of toilet soap requires the installation of expensive machinery and a greater degree of skill than is necessary in the manufacture of laundry soap. Not only the cost of plant and the superior skill required in manufacture, but the experience and ability required in marketing the product, confine its manufacture to a comparatively limited number of plants. The manufacture of toilet soap in the United States dates from 1844, at which time a Frenchman, Jules Haul, made soap of this character with very primitive apparatus, in Philadelphia. Since the original manufacture of toilet soap in the United States, just noted, American skill and experience, together with the superior mechanical appliances employed, have so far advanced that the toilet soap produced in this country is equal to that produced elsewhere in the world.

7. Although toilet soap can be made by any of the three processes previously described, the term generally has reference to what is called a *milled soap*, meaning by this a soap

that, after having been partly dehydrated, is kneaded into films of dough-like consistency in a machine called a *mill.* The soap is then compressed into an elongated bar, which is cut into sections and pressed into separate cakes.

By this process of manufacture it is possible to combine the finest style and finish with superior quality and durability. Owing to the partial dehydration to which the toilet-soap base has been subjected, its milling, and the subsequent compression in the plodder, soap manufactured in this manner is the most economical for toilet purposes.

8. Toilet-Soap Base.—The manufacture of toilet soap requires first the manufacture of what is commonly called the *toilet-soap base.* This may be either a well-made settled soap, a semiboiled soap, or a cold-process soap. The principal requirements of a good toilet-soap base are that it be made from fresh material of good quality, be free from impurities, completely saponified, perfectly neutral, and of a good, tough grain. In large establishments, the manufacture of the toilet-soap base is usually entrusted to one man having special skill in the boiling of soap for this purpose. The nature of the stock used is very important.

Good, fresh tallow, with the characteristic shortness of grain of the soap made from it, softened by the addition of suitable proportions of cottonseed oil or a good grade of white grease, and smoothed with a proportion of coconut oil, will make a first-class toilet-soap base.

9. The formulas of the toilet-soap base vary greatly. Castor oil and lard may be used to make the soap milder and to admit of a finer finish in the pressed bar. In the manufacture of cheap toilet soap—what is known in the trade as five-and-ten-cent goods—not only is material of inferior quality used, but also adulterants well known to the toilet-soap miller. A fragrant and lasting perfume may also be added. Palm oil forms an excellent ingredient of the toilet-soap base, the natural odor of the oil harmonizing well with the perfuming material.

In the boiling of the toilet-soap base, the greatest care lies in completely saponifying the stock. In the use of coconut and cottonseed oils, this complete saponification is very important, for there are no oils used by the soap maker that are more liable to become rancid, especially when present as unsaponified stock in the finished soap, the rancidity being invariably betrayed by the odor on the hands after using.

10. Boiling Toilet-Soap Base.—The manufacture of the toilet-soap base does not differ essentially from the manufacture of settled rosin soap. Too much stress cannot be laid on the facts that the stock must be pure and fresh, the kettle and all appurtenances scrupulously clean, and that completeness of saponification must be insured. Covers for the kettles are usually provided in order to keep out dirt and to hold the heat for a longer settle.

The stock change is effected as previously described, care being taken to kill the stock thoroughly, even though the stock lye may contain an excess of caustic alkali. A slight strength is desirable, as it is believed that the texture of the soap is improved thereby. After graining and settling the waste lye, the latter is run off. The soap is then boiled, or strengthened, with the addition of weak caustic lye, after which it is grained sharply with undiluted caustic lye. This strength lye is withdrawn and held in storage for use in inferior grades of soap. The soap is now boiled up with live steam, and water is carefully added until the soap shows a characteristic flat grain and is all but closed. The soap is now allowed to settle, as on the settling change in the manufacture of settled rosin soap.

11. The success of a toilet-soap settle can be determined by comparing the amount of water in the soap at the time of finishing with that of a 2- or 3-day settle. When the steam is shut off, a sample will show 40 to 47 per cent. of water; if the settle shows 30 to 31 per cent. of water, it will make good soap. Much variation from these figures will result in an

unsatisfactory product when the soap is framed. It is believed that the more completely settled a toilet-soap base is, the better adapted it is for milling, due to the separation of salts and impurities that tend to form the niger. The more thoroughly these are removed, the less liable is the soap to come from the plodder in a cracked condition. At the expiration of the settling period, the soap, if no filler is added, is pumped directly into frames.

12. The nature of the process to be used in the preparation of the toilet-soap base and the care to be taken in the operation are determined by the quality of the product desired. For cheap, milled soaps, a base made by the cold process may be used, but more generally one made by the semiboiled process is used. With the latter process, the soap should be carefully settled; then the niger, if stock of good quality is used, can be incorporated in a succeeding boil or, preferably, added to a kettle charge for laundry soap. The soap is framed in the regular way and when cold is ready for cutting.

In the manufacture of hard soap, free from filling, whether by the settled, the semiboiled, or the cold process, the yield is commonly estimated as 50 per cent. This, therefore, gives the toilet-soap base, by whatever process it is manufactured, a water content varying from 30 to 33 per cent. To insure a satisfactory product on milling, this percentage of water must be reduced about 50 per cent. With settled soap for laundry purposes, the water content was reduced from 3 to 5 per cent., just sufficient to permit a good finish on pressing and stamping.

13. Preparation of the Toilet-Soap Base for Milling. In preparing the toilet-soap base for milling, the frame of soap is cut into long bars of such dimensions that the preliminary drying is effected in the quickest manner. At this stage it is merely desired to dry the soap, so that it can be reduced to chips in a cleanly manner. The superficially dried bars of soap are laid lengthwise in the feed-box *a* of the automatic chipper shown in Fig. 3, when they fall by gravity against the

knives set in the radial slits *b*, two of which are shown. The soap can be cut into chips of any desired thickness by adjusting the knives at varying distances above the surface of the disk *d*, which is rotated by a pulley on the shaft *c*. The chips are collected on the opposite side of the machine and spread on the bottoms of trays. These are then transferred to the drying room, where they are allowed to remain until the water content has been reduced to that degree permitting the most satisfactory treatment in the milling machine.

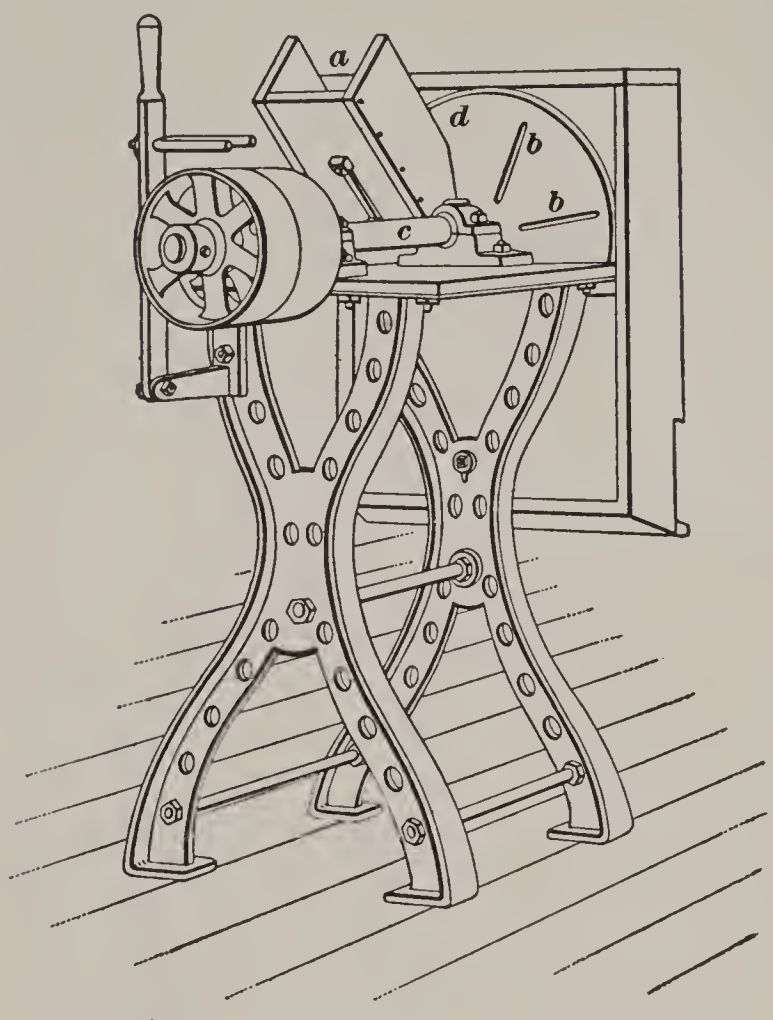

FIG. 3

14. A very convenient arrangement for the drying of toilet-soap chips is shown in Fig. 4. Air is forced over the soap contained in the trays of the case *a*, by means of the blower *b*, and escapes by means of the stack at one end. In the illustration the casing is partly broken away so as to show the location of the blower. The degree of dehydration is variable, depending on the quality of the product desired.

If cheapening material is to be added in the mill, its capacity for moisture demands that the chips be not too dry, or the soap will come from the plodder in a cracked condition. Again, with unfilled toilet soap, the consistency of the mass may be varied at will by suitable treatment during the milling process. If the soap works too dry in the mill, either softer soap of the same quality or some water may be added, according to the judgment of the miller.

The continuation of the drying process is best determined by experience. For goods of superior quality, the chips are sufficiently dry when the water content has been reduced from 30 or 33 per cent. to 15 or 18 per cent. The chips are now ready for the amalgamating and the milling processes.

15. Amalgamator.—The amalgamator consists essentially of a rectangular box, set on a frame, and equipped with a horizontal shaft through the center of which are set paddles, as in the horizontal crutcher. It has for its object the mixing of the perfume and color with the dried soap before milling, and by its use one or two millings are saved. By the old

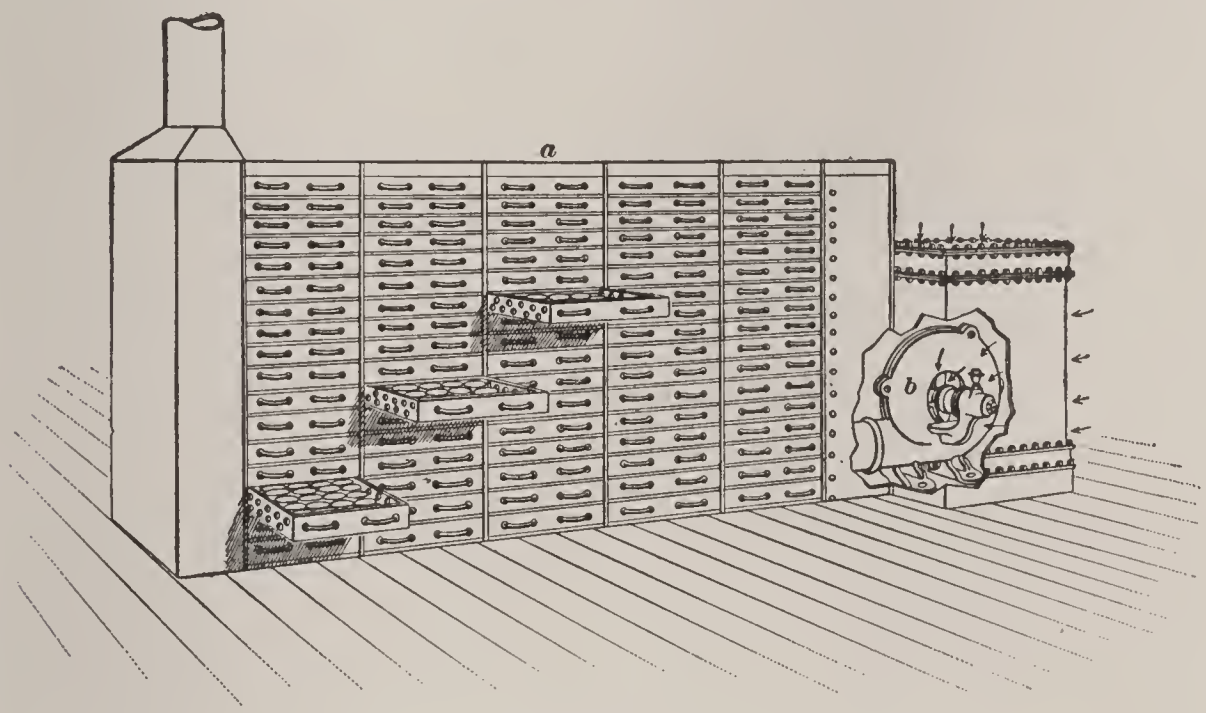

FIG. 4

method, the chips, color, and perfume were mixed in a box with a shovel. A very uniform mixture is possible with the amalgamator.

16. Toilet-Soap Mill.—The toilet-soap mill, shown in Fig. 5, consists of a hopper *a*, in which the soap to be milled is placed, set on rolls *b* and *c* of a series of granite rolls *b*, *c*, *d*, and *e*. These rolls vary from three to five in number. They are carried on heavy steel shafts, forming the core of the roll, and are mounted in the most improved machines one above the other at an angle of 45°. Granite, with a smooth and true finish, is generally used for the rolls, which

vary in diameter from 8 to 18 inches, and in length from 16 to 24 inches or longer, as desired. The capacity of the mill is rated by the manufacturer according to the amount of soap milled per hour, varying from 80 to 250 pounds for the roll dimensions just mentioned. The roll *c*, Fig. 5, is supported in stationary journals. The intervening distances between adjoining rolls may be varied at will by means of setscrews on both sides of the mill. In the illustration, the setscrews on one side are shown at *f*, *g*, and *h*. The rolls rotate on their shafts in the directions indicated by the arrows.

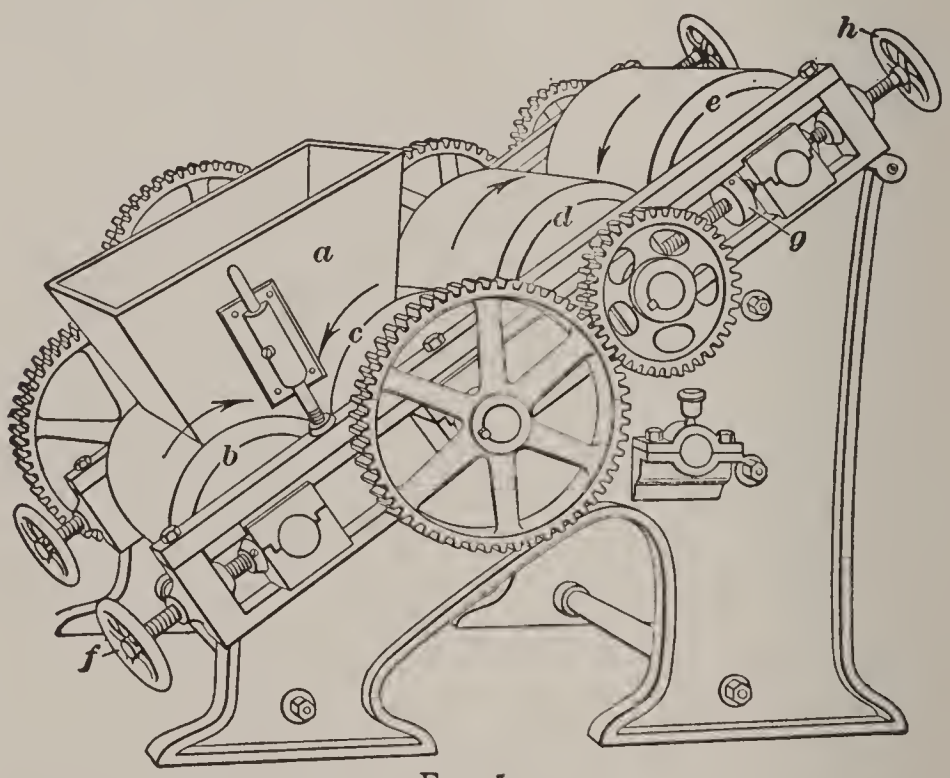

FIG. 5

17. Milling the Toilet-Soap Base.—When the chips are dried suitably and have the right feel when taken up by the handful, the amount required for a charge is introduced into the hopper and passed through the mill until reduced to a fairly homogeneous mass. One milling should suffice for this initial reduction.

During this preliminary milling, the distance between the rolls should be greater than at later stages in the milling process, owing to the coarseness of the material worked. During milling, the chips pass down between rolls *b* and *c*, Fig. 5, up between rolls *c* and *d*, and down between rolls *d* and *e*. Then,

in the condition of a thin, translucent film, they are removed by scrapers from the last roll and returned to the hopper, if desired, for another milling.

18. When an amalgamator is not used, and the proper consistency has been reached by milling, the soap is collected in a box, or trough, where the perfume and coloring matter in proportions based on the weight of the charge of soap delivered to the mill is added. If the perfume and coloring matter are in a dry state, it may be simply dusted on the soap in the mill. If liquid, they must be added to the shreds of soap resulting from the first milling and allowed to percolate through, yet not flow from, the mass. The soap is then transferred to the hopper and worked through the mill to the satisfaction of the attendant.

For cheap goods, three or four millings may suffice; for superior goods, or to produce the best possible texture in goods of any quality, seven or eight millings are required. After the milling process, the shreds of soap should be perfectly homogeneous, with the perfume and coloring matter, if any of the latter is used, thoroughly worked through.

19. Plodding Toilet Soap.—After satisfactory results have been obtained in the milling process, the soap is ready for the *plodder*. The soap as it comes from the mill is in thin, translucent laminæ. The function of the plodder is to compress this soap into a compact mass, which is expelled from the plodder in the form of an elongated bar. This bar is then cut into cakes of dimensions adapting them to the mold and die of the soap press.

20. Plodders.—The earliest form of plodder consisted of the naked hands, which molded the mass and crudely kneaded it with mortar and pestle into a globular or oblong bar.

The earliest form of machine plodder was a cylinder enclosing a screw, by means of which the soap that was fed into the cylinder at one end and above the screw was compressed. This is essentially the construction of the modern plodder. The improvements on this early form consist chiefly in

an increase and a more scientific distribution of the weight of the machine, and in the substitution of electricity as the source of power, thus permitting a greater compressive force to be applied to the soap. These mechanical improvements in the plodder have enabled toilet-soap manufacturers to produce a more compact, a more durable, and a better appearing piece of soap.

21. In the plodder shown in Fig. 6, *a* is the hopper into which the soap is placed; *b* is the case enclosing the horizontal

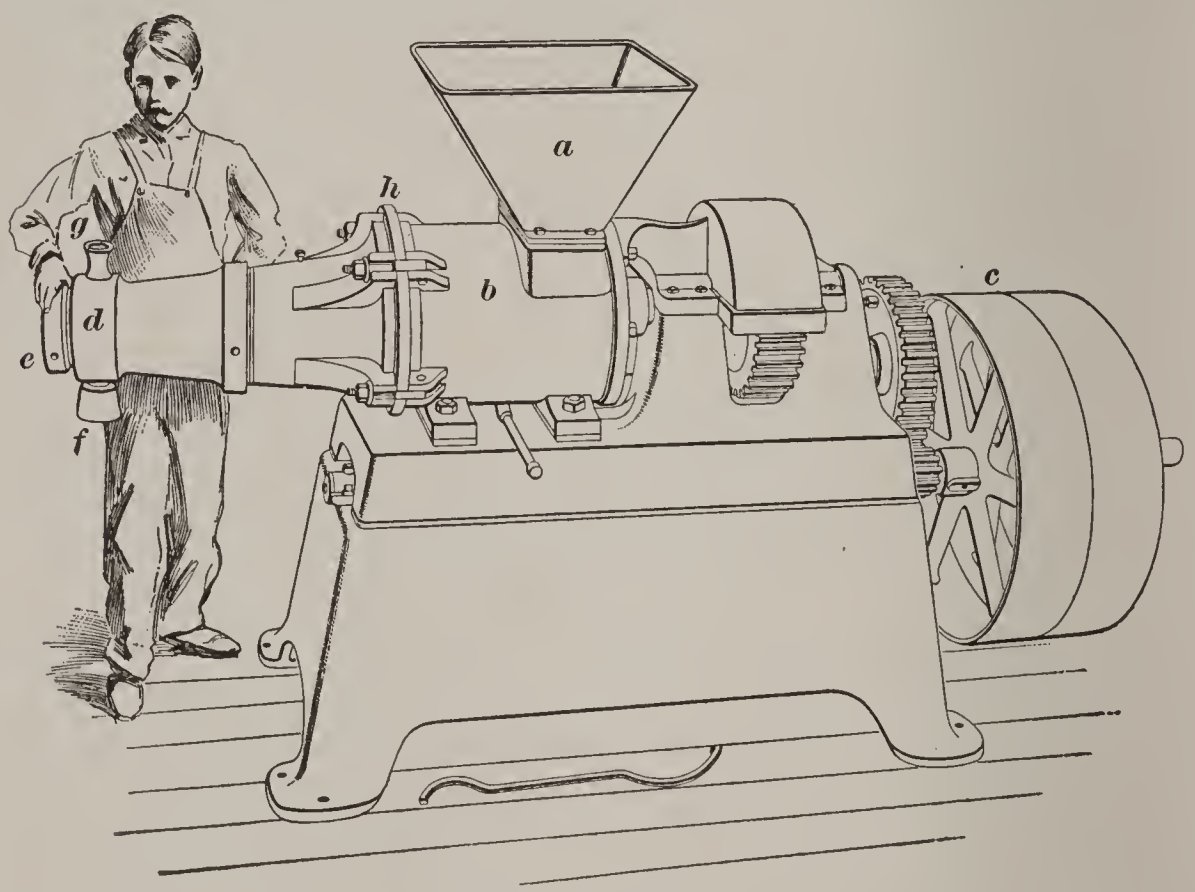

FIG. 6

screw compressor impelled by power applied by means of a belt to the pulley *c*; *d* is a concentric hollow casing enveloping the nozzle of the plodder, and is filled with water added at *g* and maintained at a definite temperature. The cake former *e* is heated by a gas flame applied at *f*, and it is screwed to the nozzle through which the elongated bar of compressed soap is forced. A sectional connection *h* of the screw case provides for the ready examination of the interior of the case. So long as soap is added to the hopper, the action of the plodder is continuous.

22. Plodders may be divided into two classes, according to the mode of applying the power, namely, the hydraulic and the motor-driven plodder. With the former, the output per day does not exceed 1,000 to 1,200 pounds of soap; with the latter, the output in the same length of time is much greater. The hydraulic plodder is being displaced by the motor-driven plodder, with its greater rapidity of operation.

The nozzle of the plodder is provided with a screw head, to permit the attachment of the cake former. With this arrangement the elongated bar is made to assume any

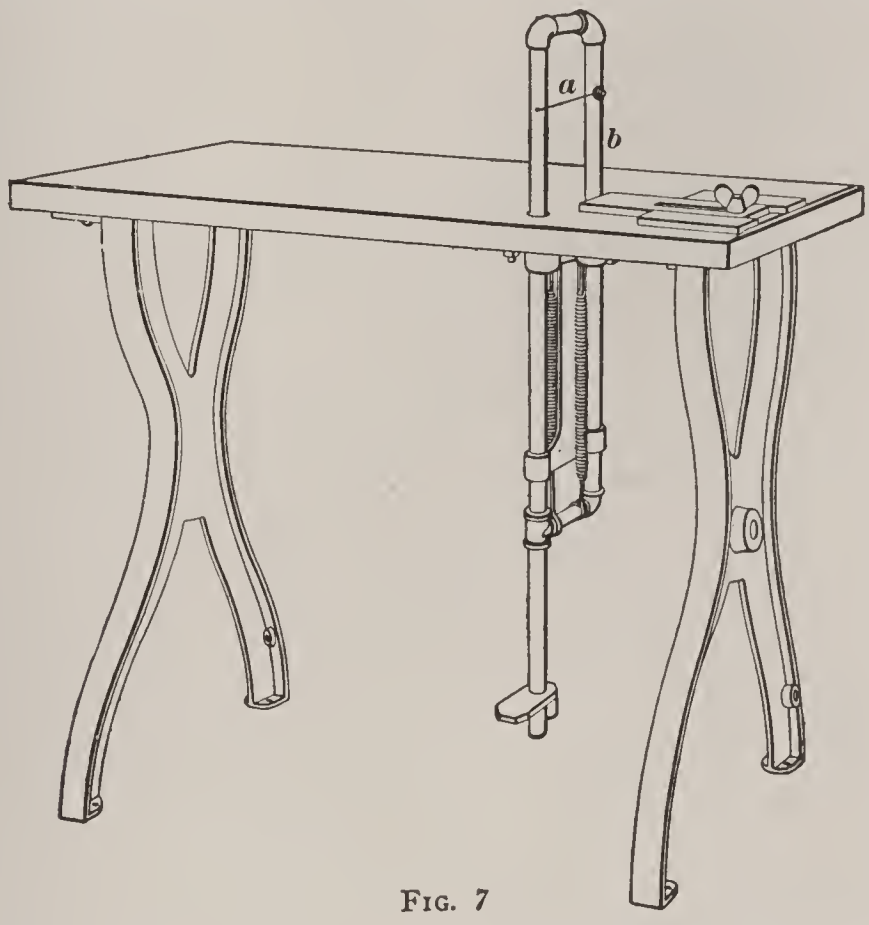

FIG. 7

cross-section desired, as circular, square, or rectangular. The purpose of the hot-water jacket, shown at *d*, Fig. 6, is to soften the soap to such a consistency that, when forced through the cake former, the cohesion of the soap mass will not be destroyed and the soap will not, as it is termed, "crack" or "splinter." Plodders are rated according to the pounds of soap capable of being plodded per day under a maximum average compressive force.

23. Cutting and Pressing the Plodded Toilet Soap. The soap as it is delivered from the nozzle of the plodder is

carried to the cutting table, shown in Fig. 7. Here, the long bar is cut into separate cakes of uniform length by the wire *a* in the movable frame *b* operated by foot-power. The experience of the attendant will determine at this stage whether it is necessary to subject the soap to a slight superficial drying in order to obtain the best possible impression on stamping. If the soap is sufficiently dry, it is taken from the cutting

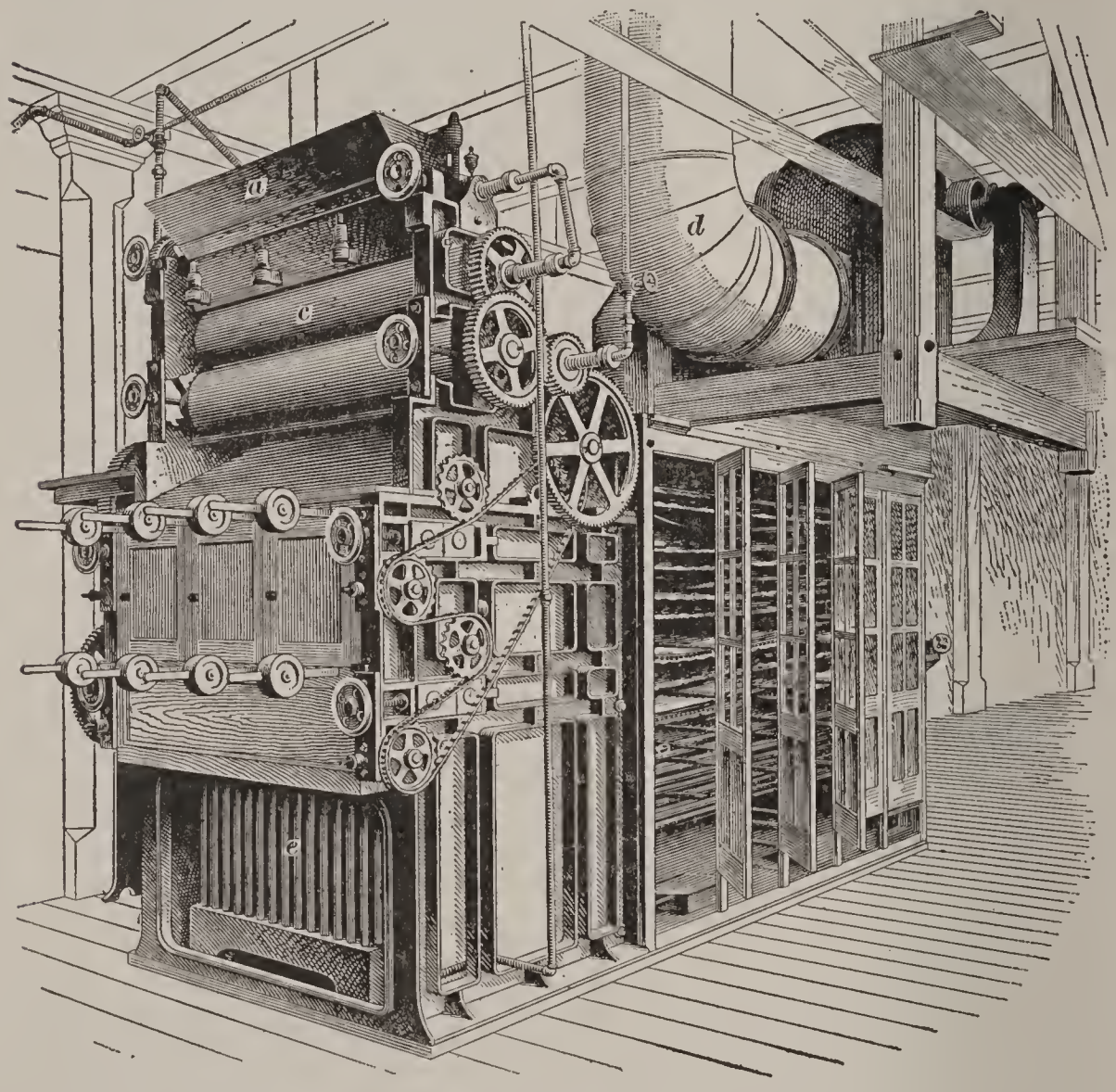

FIG. 8

table in trays to the soap press. Formerly all milled soap was pressed on old-style foot presses, but power presses have been improved to such an extent that they are now used in the larger plants. From the press, the cakes are taken to the benches for hand wrapping, or to automatic wrapping machines.

24. Continuous Crusher and Dryer.—The patented process known as the **continuous crusher and dryer**

possesses the double advantage of shortening the time of manufacture and of very materially decreasing the cost of production. In this process, instead of slowly cooling great masses of soap in bulk, the paste is treated while still hot and in a liquid state, just as it comes from the kettle. While available for household and industrial soaps, this process is used almost exclusively for toilet soaps.

In the manufacture of toilet soap by the usual process, as previously explained, the material is taken from the kettle, crushed, framed, slabbed, caked, and chipped before passing to the drying room. By this special process, however, the hot soap passes directly from the kettle to the machine in which the drying is to take place, the only intermediate step being the pumping of the soap from the soap vat to the storage tank. This is done in order to elevate the soap above the crusher and dryer and to regulate its flow into the hopper *a*, Figs. 8 and 9.

The mixing tank *b*, Fig. 9, is discarded by most users of the machine, the color and perfume being added to the dry and cold soap in the mixer *f*.

25. A boiled settled soap is usually crushed while at a temperature of from 65° C. to 70° C., but soap can be pumped to this machine at a temperature of 80° C. The soap paste passes from the hopper to the first roller *c*, Fig. 9, of the five horizontal rollers *c* to c''''. The speed and pressure of these rollers gradually increase in the order in which they are lettered, being greatest at roller c''''. The soap paste striking the rollers curdles at once and gets crushed into thin layers, which a knife divides into ribbons. The soap leaves the rollers c'''' as a thin ribbon, or film, and falls on an endless band of wire gauze circulating in the drying chamber. These bands are shown through the open doors in the side of the apparatus, Fig. 8. The time required for the soap to pass from the hopper through the dryer to the box *d*, Fig. 9, is only about 12 minutes, during which period it travels the full length of the dryer a number of times, falling from one wire band to another.

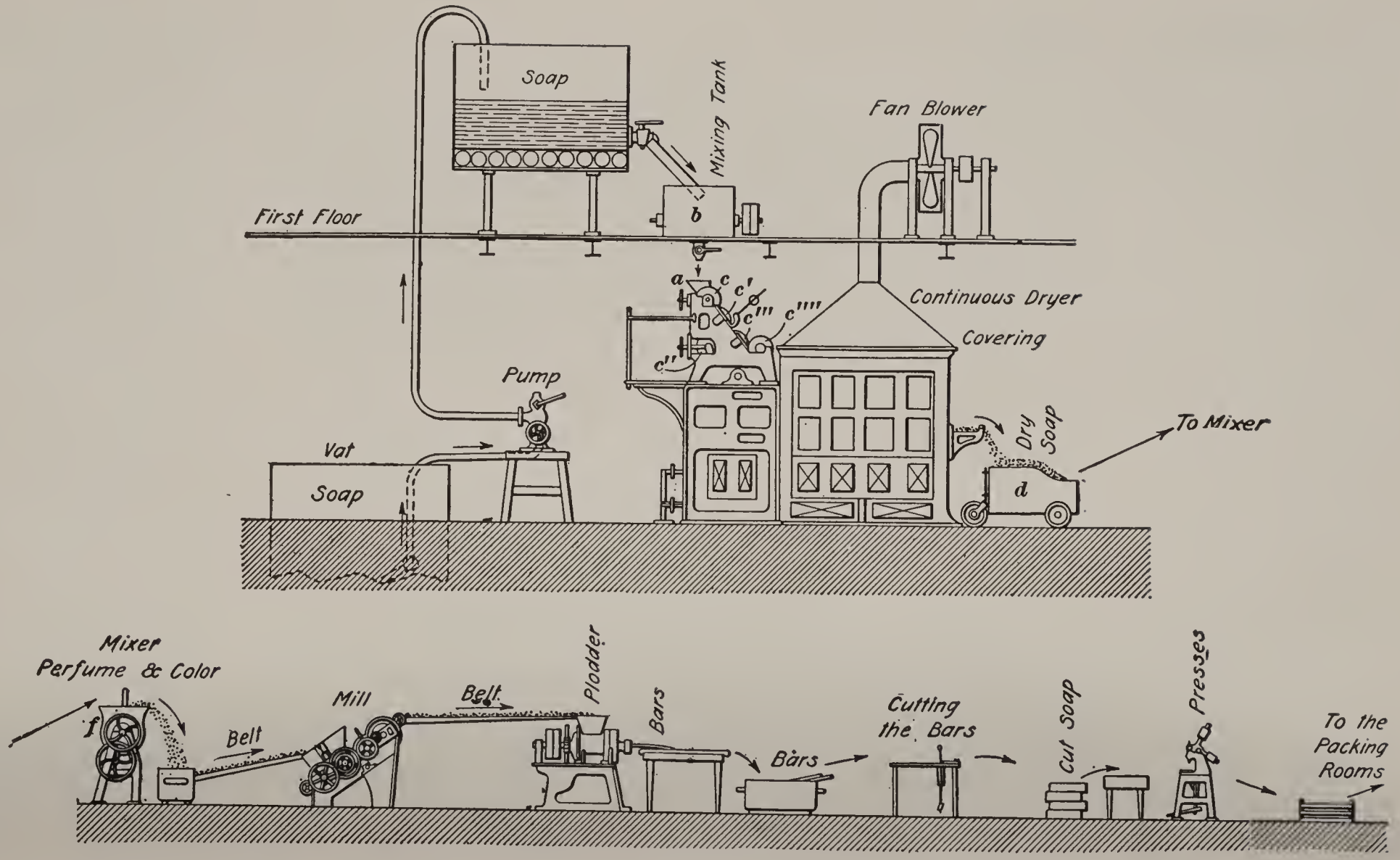
Soap
Mixing Tank
Fan Blower
First Floor
b
a
c
c'
c''
c'''
c''''
Continuous Dryer
Covering
Pump
Vat
Soap
Dry Soap
To Mixer
d
Mixer
Perfume & Color
f
Belt
Mill
Belt
Bars
Bars
Cutting the Bars
Cut Soap
Presses
To the Packing Rooms

FIG. 9

The dryer is heated by the steam coil *e*, Fig. 8, and the hot and moist air passes away through the pipe *d*. The temperature maintained in the dryer is about 35° C., as this has been found to give the best results.

These machines are constructed in various sizes, and their output ranges from 250 to 800 pounds per hour.

PERFUMING OF SOAP

PURPOSE OF PERFUMING

26. Competition in the toilet-soap business has reduced the profit to a very small margin. One important characteristic of this business is the manner in which the goods are put on the market. An attractive wrapper and an agreeable perfume are demanded by the inexperienced buyer of this class of soap to the exclusion of the essential qualities. By means of coloring matter and suitably blended essential oils, a milled soap made from very inferior stock may have its original inferiority completely obscured.

27. The blending of essential oils is a recognized art, whose development requires the constant attention and study of the skilled perfumer. The demand is always for something new, to supply which the toilet-soap manufacturer is often hard pressed. Organic chemistry has supplied the perfumer with a large and increasing number of artificial perfumes, which often surpass the natural source in intensity of fragrance and cheapness. Some of these, as nitrobenzene, or oil of mirbane, a cheap and efficient substitute for the oil of bitter almonds for perfuming laundry soap, are obtained from coal tar; others, as vanillin, borneol, menthol, eugenol, ionone, heliotropin, etc., are prepared synthetically; certain others are isolated from essential oils, as safrol, from oil of camphor, which has practically displaced the natural oil of sassafras as a soap perfume; citral, from oil of lemon; carvol. from oil of caraway; etc.

PERFUMES USED IN LAUNDRY SOAPS

28. The following list of essential oils comprises those most commonly used for perfuming laundry soap. As has been noted, the proportion used seldom exceeds $2\frac{1}{2}$ pounds per frame of 1,200 pounds of soap.

Oil of caraway seed.

Oil of cassia, with guaranteed percentage of cinnamic aldehyde.

Oil of cedarwood.

Oil of citronella.

Oil of mirbane, artificial, with odor of oil of bitter almonds.

Oil of rosemary.

Safrol, artificial oil of sassafras.

Oil of eucalyptus

Oil of thyme.

29. The best way to ascertain the most satisfactory combination of essentials oils for a laundry-soap perfume is to prepare a number of mixtures to be used experimentally as a

TABLE I

FORMULAS FOR PERFUMING OF LAUNDRY SOAP

Essential Oils	Formula 1 Parts by Weights	Formula 2 Parts by Weights
Safrol	23	27
Cedarwood	12	10
Cassia	9	7
Lavender	10	10

basis, or vehicle, for a highly fragrant and strong-bodied essential oil, as artificial oil of sassafras, or safrol. This particular oil commends itself because of its cheapness. Its fragrance may be modified by mixing it in varying proportions with other essential oils, not debarred by their high cost, until a mixture is obtained that is at once cheap, lasting in fragrance, and disguises most completely and agreeably the odor associated with the soap in use.

After two or three mixtures of equal satisfaction are obtained experimentally, the mixtures may be subjected to practical tests by studying results when they are mixed in regulated proportions in successive frames of soap.

The formulas in Table I represent two mixtures, No. 2 being modified from No. 1 as the result of an advance in the price of cassia oil. Equally satisfactory results were obtained from both mixtures.

30. Laundry soap is seldom colored, indigo paste being the only color that is used to any great extent. The blue soap thus produced often misleads the consumer into the idea that bluing is being added at the same time that washing is being done. Unbleached palm oil is the cheapest and most efficient available agent to disguise the odor and color of rosin. Very small quantities of ultramarine are used in some cases to heighten the whiteness of floating soaps. Disinfectant and tar soaps are colored, the former variably, the latter with pine tar.

PERFUMING OF TOILET SOAP

31. The direct application of the perfuming material to the mass of thin, shredded soap, after its preliminary treatment in the mill to obtain homogeneity, involves no especial difficulty. A weighed or measured quantity of perfume is simply added to the mass in the box in which the shredded soap accumulates as received from the mill, and the perfume is then incorporated sufficiently with the soap to enable the attendant to transfer it to the hopper of the mill without waste.

The blending of perfuming material to obtain desired odors, generally those imitating the natural odors of fresh flowers, constitutes a distinct art and requires for proficiency an intimate knowledge of the chemistry of essential oils and experience in working with them. The various ingredients of the perfumed stock may be bought separately and then compounded or blended by the perfumer, or they may be bought already blended from dealers in essential oils and perfumers' materials.

32. With the exception of musk and civet, which are excretory secretions of the animals producing them, the raw materials of soap perfumery consist chiefly of essential oils obtained from wood, as oil of cedarwood; from bark, as the oil of wild cherry; from foliage, as oil of eucalyptus; from fruit or seed, as oil of caraway; and from flowers, the chief source, as oil of rosemary.

There is a large and increasing number of synthetic preparations and isolated bodies possessing in a marked degree the fragrance of the natural source that now successfully compete with the latter. These bodies, as a rule, are the odoriferous principle of the natural oil, and for purposes of perfumery are not encumbered with the non-essential ingredients present in the natural oil. A correspondingly smaller quantity can be used to effect the same results and thus generally reduce the cost of production.

33. The fractional distillation of essential oils obtained from plants has shown that they are composed of a nearly odorless vehicle, consisting of one or more hydrocarbons of the terpene class, a principal odorous constituent, which may be an alcohol, phenol, aldehyde, ketone, ether, or ester, and smaller quantities of various other compounds. These modifying constituents may vary in amount in oil obtained from different parts of the same plant.

COLORING OF TOILET SOAP

34. The operation of coloring is carried out in the amalgamator, in which the coloring matter, either dry or in solution, may be added to the soap. If an amalgamator is not used, the coloring matter may be added to the soap in the mill hopper or it may be spread out on the thin layer of soap as it passes on to the rolls of the mill. If it is deemed desirable, it may also be added directly to the soap in the box at the end of the mill after the soap has had a preliminary milling.

The application of the coloring material in solution is preferable to using material in the dry state, as it admits of a

more homogeneous distribution of the color in the shortest time. There should be a consistency between the nature of the coloring material used, the odor of the perfume, the character of the soap, and the name applied to it.

35. The organic coloring materials commonly used are obtained from coal tar and receive trade names that give no indication of their composition to the purchaser. Red, pink,

TABLE II

COLORS USED IN SOAP AND CHIEF MATERIALS FOR PRODUCING THEM

Color	Material
Red	Coal-tar colors: vermilion, Venetian red, alkanet, bole, colcothar, cinnabar, chrome red, carmine.
Orange and yellow	Coal-tar colors: chrome yellow, cadmium yellow, curcumin, gamboge, turmeric.
Green	Coal-tar colors: ultramarine green, chlorophyl extract.
Brown	Coal-tar colors: brown oxides of iron, mixed blue and yellow colors.
Blue and lilac	Coal-tar color: ultramarine blue.

orange, yellow, green, brown, blue, and lilac colors are obtained direct from the makers or already compounded from dealers in perfumers' materials and with guaranteed solubility in definite parts of hot or cold water. The primary qualifications of a soap dye are inertness to the action of alkali and permanency under the conditions in which the soap is used.

In Table II are given the chief materials used for producing various colors used in the coloring of toilet soap.

The intensity of the color is determined by the amount of dye used and the character of the soap. Coconut oil, for instance, as an ingredient of a toilet-soap base will permit of greater brilliancy than would be possible without its use.

MANUFACTURE OF SOAP POWDER

36. The manufacture of soap powder in recent years has grown into a business of considerable magnitude. The earliest of those engaged in its manufacture found the business extremely profitable, but with growing competition the margin has been considerably reduced. Well-made, settled, resinous soap can be filled with upwards of 10 per cent. of soda-ash solution with good results. If this filling is increased in quantity until present in the mixture greatly in excess of the soap, a compound results which, when reduced to a finely divided state, constitutes the soap or washing powder of trade. The first consideration in the manufacture of soap powder is the composition of the soap base. Any glyceride soap stock is available for this purpose. A good soap-powder soap can also be made by using corn or cottonseed oil and grease.

Rosin, which forms a soft, sticky soap, with great affinity for water, resulting in the formation of lumps in the powder, should not be used, or at best only in small proportion and in combination with a firm tallow base. The prime requisites of a soap powder are freedom from lumps, quick solubility, and uniformity of size of the particles composing it. Some soap powders are more finely divided than others, the degree of pulverization being determined by either the fancy of the manufacturer or the demand of the trade.

37. All soap powders are mixtures of soap, soda ash, and water, and vary only in the percentages of these ingredients and the kind of soap used in their preparation. They are divided into two classes, depending upon the amount of water present, and are called *old style* and *fluffy*. The old style contains 10 to 20 per cent. of water and the fluffy 30 to 40 per cent. Typical

analyses are given in Table III. With the old-style powder the lumps are coarse and harder because sufficient water is not present to form sal soda ($Na_2CO_3 \cdot 10H_2O$) with all of the soda ash (Na_2CO_3) present. For this reason considerable heat is felt when wet hands come in contact with it. This is its chief objection. The fluffy powder contains sufficient water to form sal soda with all of its soda ash and is soft to the touch. It occupies considerably more space than the old-style powder.

38. Manufacture of Old-Style Powder.—In the manufacture of old-style powder, the soda ash, soap, and hot water are dumped into a mixer of the horizontal crutcher type and mixed until the product is lumpy. A mixer charge is usually

TABLE III
ANALYSES OF SOAP POWDERS

	Old Style		Fluffy		
	1	2	3	4	5
Moisture	13.33	14.30	34.66	37.92	40.30
Dry soap	15.12	27.80	23.47	30.15	20.61
Sodium carbonate	71.55	57.90	41.87	31.93	39.09

based on the bag of soda ash, which weighs 300 pounds, as a unit. The lumpy material is then discharged from the mixer and raked through screens to break it up and to cool it as much as possible. It is then shoveled onto trays that have high sides. These trays are then piled up in a well-ventilated room. About 5 hours is required to set the powder under the best conditions. It is then ready for milling.

39. Manufacture of Fluffy Powder.—Fluffy soap powder is made by a continuous process. The material as it comes from the mixer falls upon a series of hollow rolls through which cold brine circulates. The rolls are arranged one above the other so that the thin layer of powder which is scraped from the upper roll, after it has made one revolution,

falls on the second roll, and so on until the powder is cold and crystallization is complete. The powder is then put through a screen, weighed, and packed.

40. Soap Base.—As a soap base, any settled or semiboiled non-resinous soap may be employed. If corn or cottonseed oil is used, the soap, after saponification, is grained with caustic-soda lye, which is later drawn to a kettle that is taking a stock change for a settled soap. The alkaline strength is then used up in saponifying part of this stock. If circumstances do not warrant the separation of glycerine by graining the soap, a semiboiled soap composed of simple ingredients will satisfy every requirement.

41. Soap-Powder Mill.—The soap-powder mill is of especial importance in the manufacture of soap powder, and

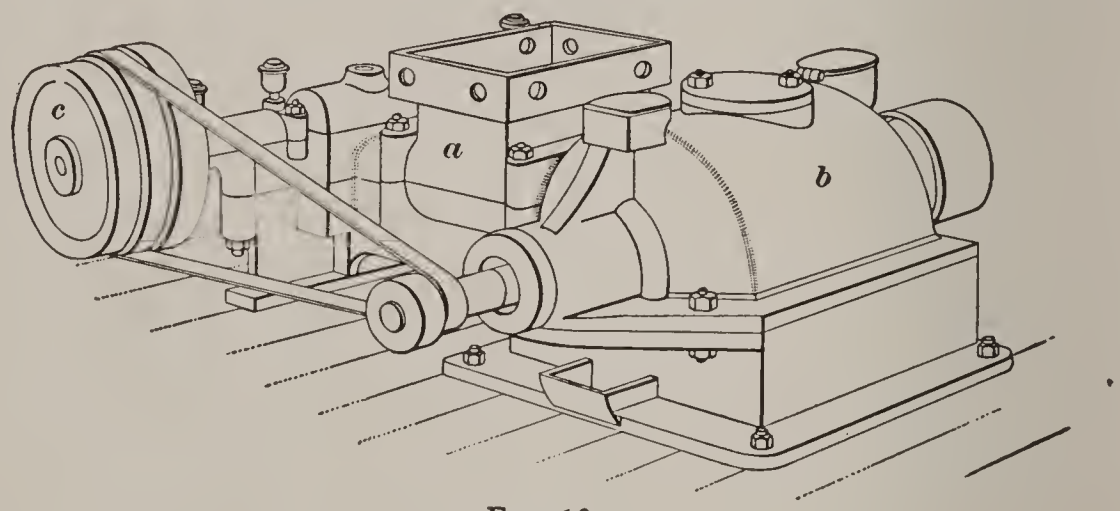

FIG. 10

should be so constructed as to do the work quickly, without heating the powder, and with a minimum of dust and repairs. The machine shown in Fig. 10 receives the trays of coarse soap powder, previously broken into lumps, in a hopper attached to the collar *a*, and crushes, grinds, and sifts it in one continuous automatic operation. The lumps are reduced by repeated blows of rapidly revolving steel blades, or beaters, enclosed in the semicylindrical casing shown at *b*. The powder is discharged through a semicylindrical screen, which serves as a sifter and which forms the under side of the casing *b*. Power is applied by belt at *c*. The mill is mounted on a well-braced framework that is completely enclosed to retain

dust and high enough to admit the introduction of a barrel to receive the powdered material. A newer style of mill employs the same principle on a larger scale, but is equipped with much greater screening surface.

42. The soap-powder department is usually arranged so that the mixers are on one floor, the mills on the floor below, and the weighing, filling, and sealing machines on the next floor below the mills. The weighing, filling, and sealing are all done automatically on special machines of which there are several types. The operations connected with soap powder making are very disagreeable because of the dust. All machines should be provided with hoods that have very strong exhausts.

43. Scouring Powder.—Scouring powder is also a soap-factory product. It is a mixture of soap powder, grit, and talc, with, at times, sal ammoniac. It requires no milling as all the ingredients are purchased in the powdered state. These are mixed, delivered by the conveyer to the weighing machines, filled and sealed into the cans or cartons. The various brands on the market differ in the amounts of their ingredients and in the kind of grit used.

RECOVERY OF GLYCERINE FROM WASTE-SOAP LYE

MANUFACTURE OF GLYCERINE

44. Historical.—Scheele, in 1779, when preparing lead plaster by heating olive oil with litharge, obtained a soluble, sweet-tasting substance, and later, in 1784, he found that the same substance could be obtained from other oils, as well as from butter and lard. To this material he gave the name *the sweet principle of fats*, and it afterwards bore the name of Scheele's sweet principle, or oil sugar.

Lead plaster is said to have been discovered by the Roman physician Menecrates about the middle of the 1st century, and also to have been known to Pliny, who briefly described

its uses, mode of preparation, and application, but nothing was known of glycerine until Scheele's day.

Later, the body was more carefully investigated by Chevreul, who determined its composition with tolerable exactitude and gave to it the name that it now bears. Pilouze in 1836 first established its formula. His experimental results corroborated Chevreul's views that the fats are ether-like compounds of the fatty acids. Henceforth glycerine became the subject of study by Berzelius, Liebig, Berthelot, and de Luca; but it remained for Wurtz to determine its exact chemical composition and relation to other bodies of the aliphatic series.

45. Scheele published the results of his investigations in a communication that appeared in the Transactions of the Royal Academy of Sweden, in 1783. He describes his method of preparation in the following terms: "It is not generally known that all solid oils obtained by pressure contain a natural sweet principle which differs in its special relations and properties from the other well-known saccharine materials occurring in the vegetable kingdom. This sweet principle makes its appearance when oils of this kind are boiled with litharge and water until the whole of the litharge is dissolved by the oil. Water is then poured upon the *emplastrum simplex* thus formed, the whole boiled for a few minutes, and on cooling the liquid is filtered off from the plaster and boiled until the residue becomes sirupy."

46. Glycerine was prepared by the foregoing process alone for many years, the lead introduced as an impurity from the litharge being removed, before concentrating the filtrate, by the use of hydrogen sulphide. This concentrated filtrate, after some primitive clarification, constituted the glycerine of commerce. Its rapidly increasing use soon demanded its production on a larger scale. It was known that in the process of soap making the glycerine liberated from the fat in the act of saponification remained in the waste lye, but efforts to recover it from this medium with the extremely crude methods used were unsuccessful.

In the meantime the manufacture of stearin candles was undergoing important developments. Numerous patents were granted for processes for the decomposition of the fats and the separation of glycerine. Gay-Lussac and Chevreul, in 1825, were the first to obtain patents. Their patent was for the alkaline saponification process, which, however, did not admit of successful operation until after the improvement by de Milly, in 1831. This is the *autoclave process* at present in use.

47. During the succeeding 20 years the sulphuric-acid distillation process was proposed and developed. Although other investigators had worked with the problem, and in fact a form of the process was in actual use, it remained for an American chemist, R. A. Tilghman, to determine the conditions productive of the most successful results. For his originality he received a patent in 1854. An English patent was soon after taken out. Tilghman's process is the one at present employed in conjunction with the use of sulphuric acid.

48. In 1847, Sobrero, in Paris, discovered nitroglycerine. Alfred Nobel demonstrated its value as an explosive in 1863 and in 1866 invented dynamite. This was followed in 1875 by blasting gelatin. The construction of vast engineering undertakings was greatly facilitated by the use of these substances, of which glycerine is the basis. The increased use of glycerine reacted directly on the source of the raw material, and the soap trade soon came to a perplexing realization of the increasing value of the product that was being daily consigned to the sewer.

49. Treatment of Waste Lye.—In the discussion of the manufacture of settled resinous soap, the progress of a boil of soap was traced, showing the formation of the various lyes. These are dilute solutions of varying percentages of sodium hydroxide, sodium carbonate, sodium sulphate, sodium chloride, and glycerine, and are contaminated by more or less soap in suspension, together with coloring matter intro-

duced by the rosin and with some mucilaginous matter or animal tissue remaining in the stock when rendered. This liquor, which often has a foul odor and is a by-product with the soap maker, now becomes the raw material of the glycerine refiner.

50. The process and apparatus used represent the culmination, in efficiency and simplicity, of all systems of glycerine recovery from waste lye. It has been declared impossible to prepare a chemically pure glycerine from waste lye—that glycerine of dynamite grade represents the limit in purity of glycerine obtained from this source. Soap lye, by the improved treatment at present in use, is made to yield a glycerine of the highest purity and answering the severest requirement of any pharmacopoeia. In the processes that have received the substantial approval of general practical use, the agents employed for the precipitation of albuminous and soapy matter and the neutralization of the alkali present in the lye are sulphuric acid, hydrochloric acid, alum, and a basic sulphate of iron.

51. The basic sulphate of iron is prepared by treating pulverized iron ore with sulphuric acid, whereby an acid salt mixed with some uncombined ore and acid is obtained. This mixture is subsequently subjected to a high temperature, namely, 380° to 500° F., when it undergoes a transformation into a basic sulphate of iron. The efficiency of basic sulphate of iron as a clarifying agent depends on the formation of ferric hydrate and insoluble iron soaps that entangle completely the albuminous matters, all of which in settling through the liquor clarify and decolorize it.

52. The waste lyes from the stock and wash changes are run into storage tanks situated in a convenient place below the soap kettles and above the treatment tanks so as to save pumping. Before they can be evaporated, the alkali must be neutralized to prevent frothing when boiled. The treatment also removes the mucilage and tissue. There are two general methods, one of which is a patented process that uses the

basic sulphate of iron previously described. The other one neutralizes about three-quarters of the alkalinity with hydrochloric acid, and the remainder with alum. The precipitated iron hydroxide in the first method and the aluminum hydroxide in the second do the coagulating and clarifying. In any treatment used, the lye is left after treatment very slightly alkaline, usually about .02 per cent.

53. Basic Sulphate-of-Iron Method.—The waste lye is run into the treatment tank and stirred with compressed air. A sample is taken and its alkalinity determined. The amount of basic sulphate of iron needed is dumped into the tank and the air turned on to keep it well agitated. In 20 minutes a sample is taken, filtered, and the alkalinity again determined. When the alkalinity is correct, the tank is emptied by pumping through a filter press into another storage tank from which the evaporators are fed.

54. Hydrochloric Acid and Alum Treatment.—The procedure is the same as that just described, except that three-quarters of the alkalinity is neutralized with hydrochloric acid and the remainder with alum. The operators in the glycerine plant are given tables by which the amounts of these chemicals needed for the alkali content are read off directly.

The entire glycerine recovery is controlled by a few simple chemical tests and the solutions and apparatus needed are placed in the glycerine-plant office. The use of these is taught to the men operating the treatment tanks, evaporators, and stills, so that the routine control work is taken out of the main laboratory, which is then concerned only with the more difficult work of testing the finished glycerine.

55. Evaporation of Treated Lye.—The next step is to remove the water and salt and concentrate the glycerine into what is known as *crude*. The crude contains from 77 to 85 per cent. of glycerine. This is done in an evaporator especially designed for the work. The evaporators are built in single or multiple effects. By multiple effects is meant, that the steam chest of the second effect receives its steam from the vapor

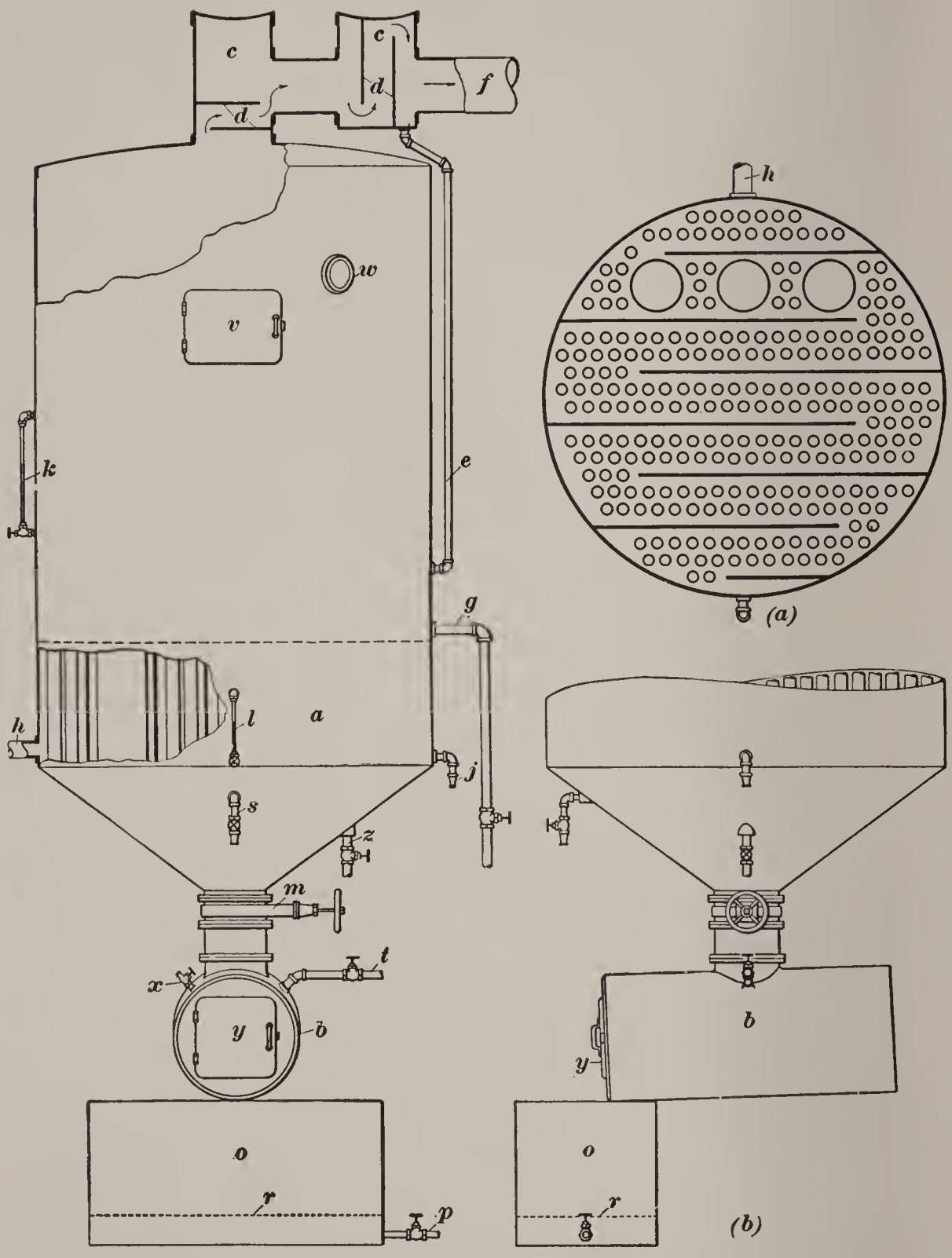

FIG. 11

line of the first effect. These evaporators are operated under a high vacuum, say 27 to 28 inches.

The evaporator shown in Fig. 11 is of the single-effect type. The process is the same with any number of effects, and for descriptive purposes the single effect is less confusing. It is a large tank built of steel plates. A steam chest *a* consisting of numerous small tubes to allow the circulation of the boiling liquor, and two or three larger tubes to increase this circulation, is built into the lower part of the evaporator. This arrangement also allows the salt, which is thrown out of solution as the concentration increases, an easy means of passing down into the salt drum *b*. The small drums *c* are placed at the top of the evaporator and fitted with baffles *d* to catch any entrained liquor and to return it by the line *e* to the evaporator. The vapors are removed by the line *f*, which is also connected with the pump which maintains the vacuum.

56. The treated lye is fed into the evaporator through the line *g*, Fig. 11. The steam chest is supplied with steam through the line *h*. For all light liquors, the boiling is done with exhaust steam, and, as it gets heavier, live steam must be used. The condensation is removed by the drip *j*. The height of the lye in the evaporator is controlled by the sight glass *k*, which is usually fitted with two bands to mark the upper and lower levels to be carried. The condensation in the steam chest is noted by the sight glass *l*, while *w* is a plate-glass window through which the boiling can be observed.

The bottom of the evaporator is fitted with a flange on which a large valve *m* is bolted, and below this valve is hung the salt drum *b*. A tank *o* is placed under the salt drum to catch and dry the recovered salt. This tank has a false bottom *r* which is connected with a pump *p* for drawing off as much lye as possible from the salt. The salt drum is provided with a vacuum line *t*. At some convenient place on the lower part of the evaporator handy for operation, a draw-off connection *s* is fitted for sampling. Fig. 11 (*a*) is a plan view of the top and bottom tube sheets of the steam chest, and (*b*) is a side elevation of the evaporator, showing the pitch of the salt

drum. The entire evaporator and lines are heavily insulated to conserve the heat.

57. Operation of Evaporators.—All the valves of the evaporator, Fig. 11, are closed except *j* and *m*, and that on the line *f*. A vacuum of 27 to 28 inches, or the capacity of the pump, is drawn and maintained. The valve on the line *g* is opened and lye drawn to the upper mark on the glass *k*. Steam is turned into the steam chest and the boiling continued with fresh additions of the lye as it boils down. With soap lyes containing between 3 and 4 per cent. of glycerine and varying amounts of salt, not much change is noticed for a few hours, but as the concentration of glycerine progresses, the salt is precipitated and in settling forces the lye out of the salt drum *b*. When the evaporation has continued for several hours, the valve *m* is closed, the vent *x* opened slowly to break the vacuum, and the door *y* is opened to drop the salt into the tank *o*. Some of the salt will run out, but most of it must be removed with a hoe. The boiling is not interrupted. The door facings are washed with water to make a perfect joint; this door *y* and the vent *x* are closed. A vacuum is drawn on the salt drum *b* through the pipe *t*, and when the vacuum of the drum equals that of the evaporator, the salt valve *m* is opened slowly, and the boiling-down process continued. This may be finished as a crude of 75 to 85 per cent. of glycerine, which is discharged to tanks through the pipe *z*. This crude has a specific gravity of about 33° Bé.

It is here that practice varies. The evaporators are usually made up of several units and are put on a schedule of *salt drops* and *lye drops* that are staggered in time, so as to keep the work continuous. The evaporation is carried to a *half crude* as one step and finished to crude as the second.

Smaller evaporators are used for the second step. Table IV shows to what extent the glycerine content of the liquor is increased, and the salt and sodium sulphate content is decreased, by evaporation.

To save as much heavy lye as possible and also to facilitate handling back to the soap kettles, the salt is made very dry

by the pump on the line *p*. At some factories the drying is done in centrifugals. Thus far the main object has been to

TABLE IV

EVAPORATOR LIQUORS

Degrees Baumé	Glycerine Per Cent.	Salt Per Cent.	Sodium Sulphate Per Cent.	Boiling Point Degrees C.
27.9	19.00	19.73	3.51	109
27.8	23.44	18.86	2.33	109
28.0	29.44	17.34	1.78	112
28.3	35.21	16.29	1.29	111
28.7	43.68	14.32	.82	113
29.5	56.17	12.52	.80	116.
33.4	81.90	6.82	.51	162
33.8	81.75	7.08	.22	167

remove, as far as possible, all water and salt from the lye and concentrate the glycerine in the crude.

TREATMENT OF CRUDE GLYCERINE

58. Crude Glycerine.—Crude glycerine contains from 75 to 85 per cent. of glycerol, about 6 per cent. of salts, chiefly sodium chloride, about 5 per cent. of organic matter, constituting the *foots* obtained on subsequent distillation, while the remainder is water. It is a thick, viscous liquid, its color and clearness depending in a great measure on the character of the stock and the efficiency of the preliminary treatment that the fresh lyes have received for the removal of organic matter, including iron salts of the organic acids.

59. Distillation of Crude Glycerine.—The crude glycerine is withdrawn into storage tanks, from which it is transferred, as required, to another vacuum apparatus in which the dillation is conducted. This apparatus comprises a large cylindrical sheet-iron tank, in which the crude glyc-

erine is distilled, and a series of vertical pipes terminating at the bottoms in horizontal cylindrical reservoirs, in which the distillate condensed in the vertical pipes collects. These reservoirs are termed *catch-alls*. A still 3 feet 6 inches in diameter and 6 feet high will have about seven catch-alls which may vary from 18 inches near the still, to 30 inches in diameter at the end of the system, all being about 5 feet 6 inches long. These catch-alls are in reality air condensers.

60. At the end of the series of catch-alls are two larger horizontal cylindrical vessels surmounted by an iron cylinder filled with water-cooled tubes, through which the more volatile portion of the distillate passes and is condensed, falling into the reservoirs below. These vessels, called *sweet-water drums*, communicate with a dry-air vacuum pump, which maintains a vacuum of about 28.5 inches throughout the system. Steam at a pressure of 125 pounds, corresponding to a temperature of 345° F., circulates in a closed coil and maintains a constant temperature.

61. Advantage of System.—The essential advantage of this system of glycerine distillation consists in the injection of expanded and reheated steam into the body of crude glycerine maintained at a high temperature. Glycerine has a boiling point of 290° C., or 554° F. Under atmospheric pressure, however, it cannot be heated to this temperature without undergoing decomposition. By reducing the pressure, as is done in a closed vessel when a vacuum is maintained, it boils without decomposition, and its vapor may be condensed unchanged. Commercial crude glycerine is very impure, the organic matter present causing difficulty in the refining process. To separate this organic matter effectually, recourse must be had to some means other than boiling at a lower temperature under reduced pressure. To accomplish this, a jet of expanded and reheated steam is introduced into the mass of crude glycerine heated to the temperature of distillation.

62. If steam at boiler pressure, namely, 125 pounds, were used directly for distillation without being previously expanded

and reheated, its expansion in the distilling apparatus would not only greatly retard, but would practically stop, the operation. To the great loss in heat due to absorption by the expanded steam would be added the difficulty arising from its condensation. These adverse and prohibitory conditions are eliminated by the use of expanded and reheated steam, which is prepared in the following manner: Steam taken directly from the boilers is allowed to expand in a coiled pipe of larger diameter located inside of a well-insulated vessel, called a *reheater*, which is attached to each still and in many cases is larger than the still itself.

63. The steam in expanding suffers a reduction in temperature. The heat lost is restored by surrounding the coil within the reheater with the same unexpanded steam from the boiler. Steam thus treated is introduced directly into the crude glycerine, which distils without decomposition at a temperature of about 300° F. Before introducing the steam, crude glycerine is added in sufficient quantity to cover the jet pipe to a satisfactory height, as indicated by the gauge glass, and as the distillation continues, crude glycerine is added from time to time in quantities not too great to interfere with the even working of the still, never, however, allowing it to fall below the established level. If, from lack of attention on the part of the attendant, an excessive quantity is introduced, there is great danger of the entrainment of the impurities contained in the crude glycerine, which increase in quantity in the still as the distillation proceeds.

64. Crude-Glycerine Still.—In the still shown in Fig. 12, A is the still proper, B the reheater, C and C' the catch-all drums, and D the sweet-water drum. In the still A, the closed coil, shown in dotted lines, carries steam at boiler pressure, which heats the contents of the still to the temperature required for distillation. In the reheater B, steam at a pressure of 125 pounds enters through the pipe a and expands into the coil of larger diameter, which is shown in dotted lines. This expansion coil is surrounded by steam at boiler pressure entering the reheater through the pipe b, which also carries

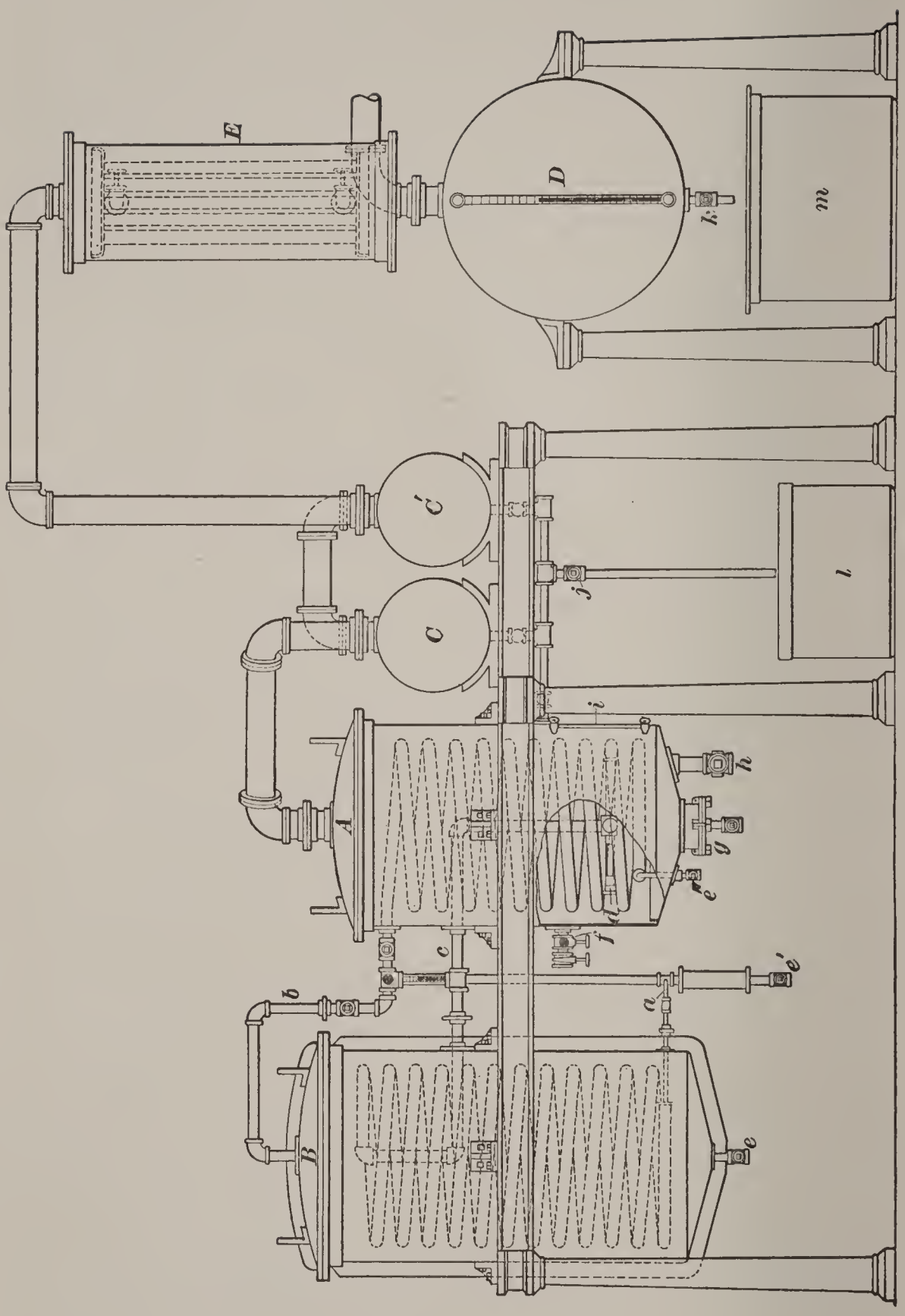

FIG. 12

steam at the same pressure into the heating coil of the still *A*. Expanded and reheated steam from the reheater enters the still through the pipe *c* and discharges into the crude glycerine contained therein through the crisscross jet shown at *d*. The catch-all stuff, so called, collects in the catch-all drums *C* and *C'*, and the lighter portion of the distillate condensed in the water-cooled jacket at *E* collects in the sweet-water drum *D*. At *e*, *e'*, and *e''* are outlets for the water of condensation from, respectively, the reheater *B*, the high-pressure steam line from the boiler, and the heating coil of the still *A*. At *f*, crude glycerine is fed into the still by suction. At *g* is the drop door through which the foots in the still *A* is discharged. Water used for washing the still is discharged at *h*. The level of the contents of the still is shown by the gauge glass *i*. At *j* and *k* are the discharge valves for the contents, respectively, of the catch-all drums *C* and *C'* and the sweet-water drum *D*. Tanks *l* and *m* are reservoirs for these respective portions of the distillate. All steam pipes leading to and from the apparatus, as well as the still and reheater, are insulated so as to retain the heat.

Before beginning a distillation, it is customary to have in stock a considerable quantity of crude glycerine, so that there will arise no necessity of shutting down the apparatus before conditions in the still render it imperative. Fresh lye is undergoing concentration all the time, and naturally the product of one operation comes in greatly reduced bulk to be the raw material of the next.

65. Tests During Distillation.—One of the chemical requirements of a dynamite glycerine is that it should not contain over .01 per cent. of salt. The best indication that a still has *boiled over*, that is, that some of the crude has been mechanically carried over to the catch-alls, is the presence of a high chlorine content in the distillate. It is possible to ascertain the amount of chlorine and control this part of the operation by providing the attendant with a simple chemical test and teaching him its use. All the catch-alls are fitted with sampling pipes. A large sample, say 50 to 100 cubic

centimeters, is obtained, a few drops of potassium-chromate solution added, the mixture diluted with distilled water, and titrated with a standard solution of silver nitrate, drop by drop, until the permanent silver chromate precipitate is formed. This silver-nitrate solution is of such strength that either 10 or 20 drops indicate the limit of salt allowed. The test is most valuable. The distillation runs a long time before dropping, say 24 to 36 hours, and it is very essential that the purity of the distillate should be known at all times. The controlling test

TABLE V

GLYCERINE DISTILLATES

Catch-All	Specific Gravity at 15.5° C.	Chlorine Per Cent.
First	1.2595	.0011
Second	1.2587	.0011
Third	1.2580	.0011
Fourth	1.2578	.0011
Fifth	1.2557	.0011
Sixth	1.2553	.0011
Seventh	1.2519	.0006
Eighth	1.2515	.0006
Ninth	1.2469	.0006
Tenth	1.2452	.0006

is made on the first catch-all, as it is nearest the source of salt. If it is very high in salt, the other catch-alls are tested, and if they all show high, the operation is stopped, the entire still and catch-alls washed out and the distillation started anew. If the first catch-all is only slightly over the limit, the distillation proceeds, as the other catch-alls will average the salt down. Table V shows the results obtained from an actual run of a 6-foot still fitted with ten catch-alls.

66. Products of Distillation.—The products of the distillation of crude glycerine may be separated into three

classes, namely, material collected in the catch-alls, technically called *distillate;* material of a much lighter gravity, called *sweet water*, consisting chiefly of water containing from no glycerine at all to as high as 12 per cent.; and a black, viscous residuum left in the still, constituting the *foots*.

67. Refined Glycerine.—The contents of the catch-alls still contain too much water and are removed to a cylindrical tank, called a *concentrator*, for further refining, which consists in the removal of water. The concentrator is provided with closed steam coils and a vacuum system. The distillate is transferred as quickly as possible from the still to the concentrator to save the heat, and the concentration is then continued. Practice dictates its length, but 2 to 3 hours is usually enough. At the end of the concentration some bone black, which acts as a decolorizer, is mixed with some of the distillate and drawn into the concentrator. The glycerine is then pumped through a small filter press that discharges directly into a covered tank. It is drummed at once from this tank, allowed to stand overnight to cool, and the drums filled up the next day.

Glycerine in any concentrated form must be handled very hot. Added to the slowing up in flowing when cold, is the danger of breaking the filter plates when cold glycerine is forced through them.

68. Sweet Water.—The material known as sweet water is concentrated to the consistency of crude glycerine and is then distilled and the distillate concentrated, as explained for refined glycerine. Another use is to take it back into an evaporator that is sluggish in its boiling to dissolve the salt that collects on the tubes of the steam chest. It saves the use of water for this purpose.

69. Foots.—There remains to be considered the black residuum, or foots, in the crude-glycerine still. All the organic matter not removed in the preliminary treatment of the lye accumulates in the still and forms this black, viscous residue, which, if the distillation is carried too far, becomes so hard that it is removed from the still only with great diffi-

culty. To facilitate its easy handling and the recovery of the large quantity of glycerine retained by it, the distillation is checked at that stage beyond which there is danger of contaminating the distillate with entrained matter from the still. The quantity of glycerine present in the foots depends on the concentration, and is about 50 per cent.

In the distillation of crude glycerine, the organic compounds of sodium do not precipitate as do the inorganic compounds, namely, sodium sulphate and sodium chloride, and the former, as the mass in the still undergoes concentration, remain to constitute the foots. There are present, usually, about 5 per cent. of salt, from 20 to 30 per cent. of sodium acetate, and from 10 to 15 per cent. of sodium salts of non-volatile organic acids.

70. While still soft and comparatively fluid, the foots are transferred to a tank and neutralized with sulphuric acid. After the gradual addition of the diluted acid and filtering, the product is concentrated, forming crude glycerine from foots; this is then distilled. About 1,200 pounds of foots is obtained from every 10,000 pounds of crude glycerine, yielding on distillation about 50 per cent. of glycerine.

It is the practice in some refineries to shut off the feed supply of crude for a few hours near the end of the run and to boil down the foots until they show a certain consistency in the sight glass, and then run them to the sewer as soon as the steam is shut off and the vacuum broken. The price of glycerine of course controls this procedure.

71. The glycerine obtained by the process described constitutes the dynamite glycerine of commerce. It is of a pale straw color and requires only subsequent distillation and filtration through bone black to become the water-white, chemically pure glycerine of the pharmacopoeia. Its specific gravity is an important physical characteristic, and is subject to considerable variation. A density of 1.263 at 15° C. is commonly obtained.

A sample from each run of refined glycerine is analyzed for sodium chloride, ash, carbonaceous residue on ignition, and

for acidity, both free and combined, in addition to a determination of the specific gravity. Samples, on standing, tend to accumulate color, due doubtless to an oxidation process of a nature not clearly understood.

72. Chemically Pure Glycerine.—To meet the requirements of the United States Pharmacopoeia, the dynamite grade of glycerine is distilled again and treated with bone black and filtered to make it water white. Sometimes the same object can be obtained by selecting certain portions of the first distillate, treating them with bone black, and filtering. This grade of glycerine is only required to be of 95 per cent. strength and distilled water is added to reduce it.

73. Saponification Crude Glycerine.—All crude glycerines not made by the method previously described are called *saponification crudes*. These include those recovered from the acid saponification and autoclave processes for making soap and candles. Sometimes they are called *candle crude*, or *Twitchell crude*. These crudes are concentrated from lyes containing 15 per cent. of glycerol and are easily distinguished by their low salt content. They have a specific gravity of about 28° Bé., and the best grades will contain 90 per cent. of glycerol. They are refined exactly as are soap-lye crudes and, owing to the absence of salt, are much easier to handle.

74. The chemical examination of the product, not only during the various stages of the refining process, but also at its completion, is a matter of the utmost importance. By this close watching the refiner is warned of changes too delicate for observation, and is thus able to correct in its first stages any abnormal behavior that would deteriorate the final product.

The examination of the refined glycerine not only indicates the care exercised in the refining, but forms the basis for the valuation and sale. The influence exerted by foreign matter in the glycerine on its subsequent use in nitration and the manufacture of dynamite demands a searching chemical and physical examination that is entirely warranted by the danger attending these processes.

CHEMICAL EXAMINATION OF RAW MATERIALS AND PRODUCTS

INTRODUCTION

75. Importance of Chemical Examination.—Every large soap manufactory maintains a chemical laboratory and employs chemists whose duties are to examine all raw materials, thus enabling the purchasing department to avoid losses incident to misrepresentation and to insist on a high grade of material being offered. The chemist analyzes soap and similar products made by competitors, in order to obtain the necessary information whereby his employer is enabled to duplicate it promptly, if desired, at the same or a lower figure. He examines daily the various products that occur in routine factory work and promptly informs the superintendent of conditions requiring modification or elimination. Glycerine recovery cannot be carried on with complete satisfaction without some knowledge of the chemical principles involved in its formation in soap manufacture and its recovery from waste-soap lye. Refined glycerine is sold under a guarantee of its quality, to determine which skill in chemical analysis is necessary. As soap manufactories grow in size and as competition increases, the services of a chemist become more indispensable. It may be truthfully stated that the development of the soap industry to its present proportions would not have been possible without the aid of the chemist.

76. In industrial laboratory work, owing to the quickness with which the information obtained by chemical analysis is desired, many of the analytical methods given in technical treatises are seldom or never used, or only in part. In the routine laboratory work, absolute accuracy, while desired, is not required in every case, it being sufficient that successive

determinations be performed as accurately as the time will permit and that they be uniform, for with uniformity of manufacturing operations, the analytical results must be on a perfectly comparative basis.

EXAMINATION OF SOAP STOCK

77. The following methods of sampling and analysis of soap stock have been taken from the report of the committee appointed by the American Chemical Society, and, contain all the essential features of the methods embodied in the report.

SAMPLING

Tank Cars

1. *Sampling While Loading.*—Sample shall be taken at discharge of pipe where it enters the tank-car dome. The total sample taken shall be not less than 50 pounds and shall be a composite of small samples of about 1 pound each taken at regular intervals during the entire period of loading. The sample thus obtained is thoroughly mixed and uniform 3-pound portions placed in air-tight 3-pound metal containers. At least three such samples shall be put up, one for buyer, one for seller, and the third to be sent to a referee chemist in case of dispute. All samples are to be promptly and correctly labeled and sealed.

2. *Sampling From Car On Track.*[1]—(*a*) When contents are solid:[2] In this case the sample is taken by means of a large tryer measuring about 2 inches across and about $1\frac{1}{2}$ times the depth of the car in length. Several tryerfuls are taken vertically and obliquely toward the ends of the car until 50 pounds are accumulated, when the sample is softened, mixed,

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[1]Live steam must not be turned into tank cars or coils before samples are drawn, since there is no certain way of telling when coils are free from leaks.

[2]If there is water present under the solid material the fact should be noted and the water estimated separately.

and handled as under 1. In case the contents of the tank car have assumed a very hard condition, as in winter weather, so that it is impossible to insert the tryer and it becomes necessary to soften the contents of the car by means of the closed steam coil (in nearly all tank cars the closed steam coil leaks), or by means of open steam in order to draw a proper sample, suitable arrangements must be made between buyer and seller for the sampling of the car after it is sufficiently softened, due consideration to be given to the possible presence of water in the material in the car as received and also to the possible addition of water during the steaming. The committee knows of no direct method for sampling a hard-frozen tank car of tallow in a satisfactory manner.

(*b*) When contents are liquid: The sample taken is to be a 50-pound composite made up of numerous small samples taken from the top, bottom, and intermediate points by means of a bottle or metal container with removable stopper or top. This device attached to a suitable pole is lowered to the various desired depths, when the top or stopper is removed and the container allowed to fill. The 50-pound sample thus obtained is handled as under 1.

(*c*) When contents are in a semisolid state, or when stearine has separated from liquid portions: In this case a combination of (*a*) and (*b*) may be used by agreement of the parties or the whole may be melted and procedure (*b*) followed.

Barrels, Tierces, Casks, Drums, and Other Packages

All packages shall be sampled, unless by special agreement the parties arrange to sample a lesser number; but in any case not less than 10 per cent. of the total number shall be sampled. The total sample taken shall be at least 20 pounds in weight for each 100 barrels, or equivalent.

1. *Barrels, Tierces, and Casks.*—(*a*) When contents are solid: The small sample shall be taken by a tryer through the bunghole or through a special hole bored in the head or side for the purpose, with a 1-inch or larger auger. Care should be taken to avoid and eliminate all borings and chips from the sample. The tryer is inserted in such a way as to reach the head of the

barrel, tierce, or cask. The large sample is softened, mixed, and handled according to Tank Cars 1.

(*b*) When contents are liquid: In this case use is made of a glass tube with constricted lower end. This is inserted slowly and allowed to fill with the liquid, when the upper end is closed and the tube withdrawn, the contents being allowed to drain into the sample container. After the entire sample is taken it is thoroughly mixed and handled according to Tank Cars 1.

(*c*) When contents are semisolid: In this case the tryer or a glass tube with larger outlet is used, depending on the degree of fluidity.

2. *Drums.*—Samples are to be taken as under 1, use being made of the bunghole. The tryer or tube should be sufficiently long to reach the ends of the drum.

3. *Other Packages.*—Tubs, pails, and other small packages not previously mentioned are to be sampled by tryer or tube (depending on fluidity) as already outlined, the tryer or tube being inserted diagonally whenever possible.

4. *Mixed Lots and Packages.*—When lots of tallow or other fats are received in packages of various shapes and sizes, and especially wherein the fat itself is of variable composition, such must be left to the judgment of the sampler. If variable, the contents of each package should be mixed as thoroughly as possible and the amount of the individual samples taken made proportional to the sizes of the packages.

5. *Color.*—It is very important that the color of tallows be kept up to certain standards to secure a uniform product. An arbitrary color system of standards is made in the laboratory by which the melted tallow is compared and given the number which it matches the closest. A very good system of standards can be made from crude glycerine of graduated shades contained in sealed glass tubes. These tubes are of the same kind as those in which the sample is melted. They are numbered or graded from light to dark.

78. Determination of Moisture.—The standard method of determining moisture employs a vacuum oven,

but as only large laboratories are so equipped, a method comparing favorably in results is given.

Method.—Weigh out about 5 grams of the prepared sample into a tared dish. Dry to constant weight in a well-ventilated oven held at a uniform temperature between 105° and 110° C. The thermometer bulb should be close to the dish. Constant weight is attained when successive dryings for 1-hour periods show a loss of not over .05 per cent. The loss should be reported as moisture and volatile matter.

The standard dish is made of glass, shallow, lipped, and beaker form, approximately 6 to 7 centimeters in diameter and 4 centimeters deep.

The air-drying oven is not even approximately accurate for drying and semidrying oils and those of the coconut-oil group. These oils should be tested only in a vacuum oven, for which the method is the same.

A quick qualitative test for much moisture can be made by dropping some of the tallow or oil into the heated bowl of a metal spoon. If a cracking noise or frothing takes place, moisture is present. It is necessary to keep the spoon hot.

79. Determination of Free Fatty Acids.—The determination of free fatty acids is one of the most important tests applied to soap stock, as it gives not only an indication of the value of the stock as a source of glycerine, but of the care exercised in its manufacture and of its origin. The percentage of free fatty acids in soap stock varies, being greater in the summer than in the winter, owing to the fact that the agents of decomposition are more active in the former season. This is shown in Table VI.

As about 10 per cent. of glycerol is theoretically available from soap stocks, a free fatty acidity of 10 per cent. will indicate a loss of 1 per cent. of glycerol, calculated on the basis of the stock, or 10 per cent., calculated on the amount of glycerol theoretically available.

The method of procedure is as follows: Heat the sample sufficiently to melt it, and transfer 5 cubic centimeters to an

Erlenmeyer flask having a wide mouth and a capacity of 250 cubic centimeters; weigh, and add about 50 cubic centimeters of hot, neutral, 95-per-cent. alcohol. Shake well for a few minutes, then add a few drops of alcoholic phenolphthalein solution and titrate with half-normal sodium-hydroxide solution until a permanent pink color is obtained.

TABLE VI

PERCENTAGES OF FREE FATTY ACIDS

Months	Lots	Free Fatty Acid Per Cent.
January	58	4.31
February	55	4.09
March	61	4.27
April	63	5.28
May	47	5.36
June	63	6.39
July	53	8.03
August	81	8.19
September	68	7.28
October	63	7.01
November	54	5.12
December	75	4.58

Calculate free fatty acids in terms of oleic acid the molecular weight of which is 282. One cubic centimeter of $\frac{N}{2}$ $NaOH$ = .141 gram of oleic acid. Assuming that x cubic centimeters of $\frac{N}{2}$ $NaOH$ is required for neutralization, the percentage of free fatty acids may be found according to the following formula:

$$\left.\begin{array}{l}\text{Percentage of}\\ \text{free fatty acids}\end{array}\right\} = \frac{x \text{ c. c. } \frac{N}{2} NaOH \times .141 \times 100}{\text{weight taken}}$$

The free-fattty-acid determination, with alcohol as a solvent, is based on the practical insolubility of neutral glycerides in alcohol, while the free fatty acids are soluble.

By measuring a definite volume of the liquid fat, much time is saved, it being a simple matter to ascertain the average weight of 5 cubic centimeters of the soap stock usually examined.

It is customary to calculate free fatty acid to oleic acid except in the cases of palm oil, coconut oil, and palm-kernel oil. The fatty-acid content of palm oil is expressed in terms of palmitic acid while that of coconut and palm-kernel oils is expressed as lauric acid. The molecular weights of palmitic and lauric acids are respectively 256 and 200. They are both monobasic acids.

In order to obtain the best results in making a determination of free fatty acids, 95 per cent. ethyl alcohol, freshly distilled over solid caustic soda, or caustic potash, should be used. However, methyl alcohol and ethyl alcohol denatured with methyl alcohol may be substituted in routine work but they do not give as sharp end points as does ethyl alcohol.

80. Titer Test.—Soap stock of animal origin is bought and sold on the *titer*, by which is meant the highest temperature produced by the latent heat of fusion that is liberated on the solidification of the pure liquid fatty acids obtained from the stock.

To obtain reliable results by whichever modification of the method is used, it is essential that each determination be made under precisely uniform conditions and from fatty acids prepared in the same mnner. This determination may also be applied to cottonseed and coconut oils. For the former stock, it is a reliable index of the soap-making qualities of different samples of oil.

Since all tallows and greases are bought on this test, and since it is by far the most important test that can be given to a stock, it should in all cases be performed where a chemist is employed.

Standard Thermometer.—The thermometer is graduated at zero and in tenths of degrees from 10° C. to 65° C. with one

auxiliary reservoir at the upper end and another between the zero mark and the 10° mark. The cavity in the capillary tube between the zero mark and the 10° mark is at least 1 centimeter below the 10° mark, and the 10° mark is about 3 or 4 centimeters above the bulb. The length of the thermometer is about 37 centimeters over all. The thermometer has been annealed for 75 hours at 450° C. and the bulb is of Jena normal glass, or its equivalent, moderately thin, so that the thermometer will be quick-acting. The bulb is about 3 centimeters long and 6 millimeters in diameter. The stem of the thermometer is 6 millimeters in diameter and made of the best thermometer tubing, with scale etched on the stem. The graduations are clear-cut and distinct, but quite fine. The thermometer must be certified by the U. S. Bureau of Standards.

Glycerine-Caustic Solution.—Dissolve with the aid of heat 250 grams potassium hydroxide in 1,000 cubic centimeters of dynamite glycerine.

Determination.—Heat 75 cubic centimeters of the glycerine-caustic solution to 150° C. and add 50 grams of the melted fat. Stir the mixture well and continue heating until the melt is homogeneous, at no time allowing the temperature to exceed 150° C. Allow to cool somewhat and carefully add 50 cubic centimeters of 30-per-cent. sulphuric acid. Now add hot water and heat until the fatty acids separate out perfectly clear. Draw off the acid water and wash the fatty acids with hot water until free from mineral acid, then filter and heat to 130° C. as rapidly as possible with stirring. Transfer the fatty acids, when cooled somewhat, to a $1'' \times 4''$ titer tube, placed in a 16-ounce, wide-mouth bottle of clear glass, fitted with a cork that is perforated so as to hold the tube rigidly when in position. Suspend the titer thermometer so that it can be used as a stirrer and stir the fatty acids slowly (about 100 revolutions per minute) until the mercury remains stationary for 30 seconds. Allow the thermometer to hang quietly with the bulb in the center of the tube and report as the titer of the fatty acids the highest point to which the mercury rises. The titer should be made at about 20° C.

for all fats having a titer above 30° C. and at 10° C. below the titer for all other fats.

For American tallows the titer should fall between 41° and 44° C.; for cottonseed oil, between 32° and 33° C.; and for coconut oil, between 23° and 25° C. Cochin oil is usually close to 25° C. The higher the titer the more desirable the material is as a soap stock.

81. Special Tests.—For the proper identification and test for purity of fats and oils, there are numerous tests that can be employed. All the fats and oils have some chemical and physical properties that are constant between certain limits. The variations are due to locality of origin, method of extraction, refining, etc. Among these constants are the iodine value and the saponification value.

82. Iodine Value.—Fats and saponifiable oils have the property of absorbing iodine chloride because of the unsaturated fatty acids and glycerides which they contain. The percentage of iodine chloride which it absorbs, expressed in terms of iodine, is called the *iodine value* of the compound.

WIJS METHOD FOR DETERMINATION OF IODINE VALUE

83. Preparation of Reagents.—*Wijs Iodine Solution.*—(1) Dissolve separately 7.9 grams of iodine trichloride and 8.7 grams of iodine in glacial acetic acid on the water bath, taking care that the solutions do not absorb moisture. The two solutions are then poured into a 1,000 cubic centimeter flask, which is then filled up to the mark with glacial acetic acid.

Or (2) dissolve 6.5 grams of resublimed iodine in 1 liter of C. P. glacial acetic acid and pass in washed and dried chlorine gas until the original sodium-thiosulphate titration of the solution is just doubled. This solution is then preserved in amber glass-stoppered bottles, sealed with paraffin until ready for use.

$\frac{N}{10}$ *Sodium-Thiosulphate Solution.*—Dissolve 24.8 grams of C. P. sodium thiosulphate and dilute with water to 1 liter at the temperature at which the titrations are to be made.

Starch Paste.—Boil 1 gram of starch in 200 cubic centimeters of distilled water for 10 minutes and cool to room temperature.

Potassium-Iodide Solution.—Dissolve 150 grams of potassium iodide in water and make up to 1 liter.

$\frac{N}{10}$ *Potassium-Bichromate Solution.*—Dissolve 4.903 grams of C. P. potassium bichromate in water and make the volume up to 1 liter at the temperature at which titrations are to be made. One cubic centimeter = .012685 gram iodine.

Standardization of Sodium-Thiosulphate Solution.—Place 20 cubic centimeters of the potassium-bichromate solution, to which has been added 10 cubic centimeters of the solution of potassium iodide, in a glass-stoppered flask. Add to this 5 cubic centimeters of strong hydrochloric acid. Dilute with 100 cubic centimeters of water, and allow the $\frac{N}{10}$ sodium thiosulphate to flow slowly into the flask until the yellow color of the liquid has almost disappeared. Add a few drops of the starch paste, and with constant shaking continue to add the $\frac{N}{10}$ sodium-thiosulphate solution until the blue color just disappears.

Determination.—Weigh accurately from .10 to .50 gram, depending on the iodine number, of the melted and filtered sample into a clean, dry, 16-ounce glass-stoppered bottle containing 15 to 20 cubic centimeters of carbon tetrachloride or chloroform. Add 25 cubic centimeters of iodine solution from a pipette, allowing the latter to drain for a definite time. The excess of iodine should be from 50 to 60 per cent. of the amount added, that is, from 100 per cent. to 150 per cent. of the amount absorbed. Moisten the stopper with a 10-per-cent. potassium-iodide solution to prevent loss of iodine or chlorine, but guard against an amount sufficient to run down inside the bottle. Let the bottle stand in a dark place for $\frac{1}{2}$ hour at a uniform temperature. At the end of that time add 20 cubic centimeters of 10-per-cent. potassium-iodide solution and 100 cubic centimeters of distilled water. Titrate the iodine

with $\frac{N}{10}$ sodium-thiosulphate solution, which is added gradually with constant shaking, until the yellow color of the solution has almost disappeared. Add a few drops of starch paste and continue titration until the blue color has entirely disappeared. Toward the end of the reaction, stopper the bottle and shake violently so that any iodine remaining in solution in the tetrachloride or chloroform may be taken up by the potassium-iodide solution. Conduct two determinations on blanks, which must be run in the same manner as the sample except that no fat is used in the blanks. Slight variations in temperature quite appreciably affect the volume of the iodine solution, as acetic acid has a high coefficient of expansion. It is, therefore, essential that the blanks and determinations on the sample be made at the same time. The number of cubic centimeters of standard thiosulphate solution required by the blank, less the amount used in the determination, gives the thiosulphate equivalent of the iodine absorbed by the amount of sample used in the determination. Calculate to centigrams of iodine absorbed by 1 gram of sample.

To illustrate the application of the Wijs method, assume that, in making a determination, .1355 gram of linseed oil was weighed and treated with 25 cubic centimeters of the iodine solution. In a blank test 61.2 cubic centimeters of sodium-thiosulphate solution were needed for the iodine solution. In the determination 41.1 cubic centimeters of sodium-thiosulphate solution were required to titrate the excess of iodine. Therefore the iodine absorbed by the oil was equivalent to 20.1 cubic centimeters of sodium-thiosulphate solution: 20 cubic centimeters of the bichromate solution = .2537 gram iodine. It required 20.8 cubic centimeters of the sodium-thiosulphate solution in the standardization to titrate the 20 cubic centimeters of bichromate solution. Therefore,

20.8 cubic centimeters of sodium thiosulphate = .2537 gram iodine and,

20.1 cubic centimeters of sodium thiosulphate = .24516 gram iodine.

$$\frac{.24516 \times 100}{.1355} = 181,$$ the iodine value of the linseed oil used.

84. Saponification Number.—The number of milligrams of potassium hydroxide required for the complete saponification of 1 gram of fat or oil is called the *saponification number*, or *Koettstorfer number*. The reagents required are $\frac{N}{2}$ hydrochloric acid, carefully standardized, and a solution of alcoholic potassium hydroxide, prepared as follows: Dissolve 40 grams of pure potassium hydroxide in 1 liter of 95-per-cent. redistilled alcohol. The alcohol should be redistilled from potassium hydroxide over which it has been standing for some time, or with which it has been boiled for some time, using a reflux condenser. The solution must be clear and the potassium hydroxide free from carbonate.

Determination.—Weigh accurately about 5 grams of the filtered sample into a 250 to 300 cubic centimeter Erlenmeyer flask. Pipette 50 cubic centimeters of the alcoholic potassium-hydroxide solution into the flask, allowing the pipette to drain for a definite time. Connect the flask with an air condenser and boil until the fat is completely saponified (about 30 minutes). Cool and titrate with the $\frac{N}{2}$ hydrochloric acid, using phenolphthalein as an indicator. Calculate the Koettstorfer number (mg. of potassium hydroxide required to saponify 1 gram of fat). Conduct two or three blank determinations, using the same pipette and draining for the same length of time as above.

To illustrate the application of the method, assume that, in making a determination, 1.4812 grams of olive oil was weighed out and saponified with 25 cubic centimeters of alcoholic-potash solution, and that 15.2 cubic centimeters $\frac{N}{2}$ *HCl* was required to titrate back the excess of alkali. The blank required 25.4 cubic centimeters $\frac{N}{2}$ *HCl*; therefore, 10.2 cubic centimeters represents the alkali absorbed.

Calculation of Results.—

$$10.2 \times .02805 = .28611 \text{ g. } KOH = 286.11 \text{ mg. } KOH$$

$$286.11 \div 1.4812 = 193.2, \text{ saponification number}$$

Table VII gives the iodine and saponification values of some of the more common oils.

TABLE VII

IODINE AND SAPONIFICATION VALUES OF COMMON OILS

Name of Oil	Iodine Value	Saponification Value
Castor	87 to 93	183 to 186
Coconut	8.4 to 9.3	246 to 260
Corn	119 to 122	188 to 193
Cottonseed	111 to 115	193 to 195
Linseed	179 to 209	192 to 195
Olive	86 to 90	185 to 196
Palm	51 to 53	196 to 205
Palm-kernel	13 to 17	242 to 250
Peanut	96 to 103	190 to 196
Rape	99 to 103	170 to 179
Soya-bean	138 to 142	195
Tung	144 to 159	193
Tallow, beef	40.5 to 42	193 to 200
Tallow, mutton	34 to 35	192 to 195

ANALYSIS OF ROSIN

85. Determination of Unsaponifiable Matter.—The only chemical test commonly applied to rosin is the determination of the unsaponifiable matter, which increases, as previously stated, as the quality of the rosin decreases. The grading accorded the barrel from which the sample is taken is determined by comparing with standard cubes a cube cut from the sample, with dimensions equal to those of the standard. Care should be taken to have the sample cube representative of the quality of rosin in the barrel. The unsaponifiable matter present is determined in the same manner as the unsaponifiable matter in glyceride stock.

86. Comparison With Standards.—Rosin of a given grade should correspond in color and clearness with the

standard cube of the same grade. The standards should be renewed from time to time, as they tend to bleach on exposure and to lose the cube shape through softening. In comparing samples with the standards, strict uniformity of dimensions and exposure to light must be observed.

ANALYSIS OF SODA ASH

87. Determination of Sodium Carbonate.—In order to determine the amount of sodium carbonate present in soda ash, weigh 1 or 2 grams of the sample into a 500-cubic-centimeter flask and dissolve in water; add a few drops of phenolphthalein as indicator. Run in from a burette an accurately measured excess of half-normal sulphuric acid and boil to expel all traces of carbon dioxide. Titrate the excess of acid with half-normal caustic soda. The solutions are equal and are known in terms of the various sodium compounds. The weight of sodium carbonate corresponding to the number of cubic centimeters of half-normal sulphuric acid required to neutralize the soda ash multiplied by 100 is divided by the weight of alkali taken, and the result is the percentage of actual anhydrous sodium carbonate present in the soda ash.

88. Determination of Total Alkali.—To determine the total alkali present, dissolve 10 grams of the soda ash in about 150 cubic centimeters of warm distilled water and dilute to 1 liter. Remove 50 cubic centimeters of this solution to a beaker and titrate with half-normal sulphuric acid, using methyl orange as indicator. Since 1 cubic centimeter of half-normal acid is equivalent to .03082 gram of Na_2O, the percentage of Na_2O in the soda ash will be found by multiplying the number of cubic centimeters of half-normal acid required by $.03082 \times 20 \times 100$ and dividing the result by 10 (the weight of the sample taken).

ANALYSIS OF COMMERCIAL CAUSTIC SODA

89. Determination of Total Alkali.—The determination of the total amount of alkali present in commercial caustic soda is carried out exactly as explained for the determination of the total alkali of soda ash. The percentage of total alkali is expressed in terms of sodium oxide.

90. Determination of Sodium Hydroxide.—To determine the actual amount of sodium hydroxide in commercial caustic soda, weigh out about 5 grams of the sample from a glass-stoppered weighing bottle and as quickly as possible add distilled water that has previously been boiled and cooled. Transfer to a 250-cubic-centimeter graduated flask, make up to the mark and mix thoroughly. Take out 25 cubic centimeters and dilute with 50 cubic centimeters of the same distilled water. Add 3 or 4 drops of phenolphthalein solution and titrate slowly with $\frac{N}{5}$ hydrochloric acid, stirring vigorously until only a faint pink remains, and note the reading. Then add 1 or 2 drops of methyl-orange solution and resume the titration with the same acid until only a faint pink remains.

Twice the amount of acid used in the methyl-orange titration equals the amount of sodium carbonate present. The result obtained when this amount is subtracted from the total acid used indicates the amount of sodium hydroxide present.

$$1 \text{ c.c. } \frac{N}{5} HCl = .01061 \text{ g. } Na_2CO_3$$

$$1 \text{ c.c. } \frac{N}{5} HCl = .008012 \text{ g. } NaOH$$

Calculate the amount of each present in 250 cubic centimeters.

The theory on which the method is based is, that in mixtures of caustic and carbonate-of-soda solutions, the entire caustic and only one-half the carbonate are neutralized in the presence of phenolphthalein as an indicator, when the acid is added slowly to the cold solution and the latter well stirred. This is due to the formation of sodium bicarbonate ($NaHCO_3$), which

does not react with phenolphthalein but gives a complete end point with methyl orange. Therefore, the safe use of the method depends on losing none of the carbonic acid.

91. Determination of Sodium Chloride.—The lower grades of caustic soda contain salt. To determine the salt, take 25 cubic centimeters of the sample solution, add a drop of methyl orange, and make slightly acid with nitric acid. Add a slight excess of pure calcium carbonate, stir well and filter. Wash with hot water, add a few drops of a 5-per-cent. potassium-chromate solution and titrate to a slight red color with $\frac{N}{10}$ silver-nitrate solution.

1 c. c. $\frac{N}{10}$ silver-nitrate solution = .005846 g. sodium chloride.

To illustrate the method of using the results obtained by carrying out the methods of analysis for sodium hydroxide, sodium carbonate, and sodium chloride, assume that 58.4 c. c. of $\frac{N}{5}$ *HCl* were required for the phenolphthalein titration, .66 c. c. for the methyl-orange titration, and 3.7 c. c. of the $\frac{N}{10}$ silver-nitrate solution for the sodium-chloride determination.

Then, 58.4 c. c. $\frac{N}{5}$ *HCl* for phenolphthalein

.6 c. c. $\frac{N}{5}$ *HCl* for methyl orange

59.0

1.2

57.8 c. c. = sodium hydroxide

1.2 c. c. = sodium carbonate

1 c. c. $\frac{N}{5}$ *HCl* = .008012 g. sodium hydroxide

1 c. c. $\frac{N}{5}$ *HCl* = .01061 g. sodium carbonate

$$\frac{57.8 \times .008012 \times 100}{.5 \text{ (wt. of sample)}} = 92.62 \text{ per cent.}$$

$$\frac{1.2 \times .01061 \times 100}{.5 \text{ (wt. of sample)}} = 2.55 \text{ per cent.}$$

1 c. c. $\frac{N}{10} AgNO_3 = .005846$ g. of sodium chloride

$$\frac{3.7 \times .005846 \times 100}{.5 \text{ (wt. of sample)}} = 4.32 \text{ per cent.}$$

From the foregoing results, the analysis would be reported as:

	Per Cent.
Sodium hydroxide	92.62
Sodium carbonate	2.55
Sodium chloride	4.32
	99.49

This expressed in percentage of Na_2O and as degrees would make it of the 74° grade.

92. Caustic potash and pearl ash are examined in the same manner. If the quantity of potash purchased warrants the work, the percentage of caustic soda, sodium carbonate, potassium chlorides, and the alkali sulphates may be determined. These compounds are present as impurities.

ROUTINE CHEMICAL EXAMINATION OF KETTLE-ROOM PRODUCTS

ANALYSIS OF WASTE SOAP LYE

93. Determination of Total Alkali.—In order to determine the total alkali present in the waste soap lye, transfer 10 cubic centimeters of waste lye into a clean, 500-cubic-centimeter flask by means of a pipette. Dilute with 150 cubic centimeters of water, add phenolphthalein as indicator, and run in from a burette sufficient half-normal sulphuric acid to discharge the pink color. Boil to expel carbon dioxide and titrate back with seminormal caustic soda.

Illustration.—*Long Method.*—The amount of $\frac{N}{2} H_2SO_4$ required for neutralization is 1.94 cubic centimeters; 1 cubic centimeter of $\frac{N}{2} H_2SO_4$ equals .02 gram of $NaOH$. Total alkali, estimated as $NaOH$, equals $\frac{1.94 \times .02 \times 100}{10} = .388$ gram of $NaOH$ in 100 cubic centimeters of liquor.

Short Method.— CUBIC CENTIMETERS

Total amount of $\frac{N}{2}$ H_2SO_4 used is 5.90

Amount of $\frac{N}{2}$ $NaOH$ used for titrating excess of $\frac{N}{2}$ H_2SO_4 is 3.96

Amount of $\frac{N}{2}$ H_2SO_4 absorbed..... 1.94

The total alkali, estimated as $NaOH$, is $1.94 \times .2 = .388$ gram of $NaOH$ in 100 cubic centimeters of liquor.

It will be observed that these methods give the percentage of alkali by volume; the percentage by weight would be slightly less.

94. Determination of Sodium Chloride.—In order to determine the sodium chloride contained in the waste soap lye, transfer 5 cubic centimeters of waste lye into a 100-cubic-centimeter beaker by means of a pipette and dilute with 50 cubic centimeters of distilled water. Mix well and transfer 5 cubic centimeters of the diluted lye to a 4-inch porcelain evaporating dish. Now add dilute nitric acid to a slight excess, then pure calcium carbonate. Stir the contents of the dish, filter, wash with hot water and titrate the filtrate with decinormal silver-nitrate solution, using postassium chromate as indicator. Calculate the percentage of sodium chloride as if 5 grams of lye had been taken for analysis.

ILLUSTRATION.—Amount of waste lye taken is 5 cubic centimeters; amount of $\frac{N}{10}$ $AgNO_3$ required is 20.5 cubic centimeters.

$$\frac{20.5 \times .005846 \times 100}{5} = 2.35 \text{ per cent. of } NaCl \text{ (by volume)}$$

The true percentage by weight is found by dividing the preceding result by the specific gravity of the waste lye.

95. Determination of Glycerol.—As the glycerol determination requires some time, it is only done when special information as to the glycerol content of a particular lye is desired, or when crude glycerine is being purchased, on glycerol content, for refining. The analytical methods used industrially are based on the complete oxidation of glycerol to carbon dioxide and water. Potassium bichromate and sulphuric acid are used to effect the oxidation. In another, the

acetin process, the quantitative determination of the glycerol is based on its transformation into glyceryl triacetin, in accordance with the following equation:

$$2C_3H_5(OH)_3+3(CH_3\cdot CO)_2\cdot O=2C_3H_5(CH_3COO)_3+3H_2O$$

This method, when carried out by a chemist who is skilled in its operation, gives the most accurate results. One great source of error in all the oxidation methods for the determination of glycerol is the danger of oxidizing organic impurities that are incompletely removed from the solution. As a result, all oxidation methods give uniformly high results. In the acetin method, only the glyceride is susceptible to the action of the acetic anhydride.

96. Acetin Method.—When the **acetin method** is employed, about $1\frac{1}{2}$ grams of crude glycerine is heated with 7 or 8 grams of acetic anhydride and 3 grams of anhydrous sodium acetate. The function of the last reagent is to absorb water. The mixture is gently boiled for $1\frac{1}{2}$ hours in a flask provided with a water-cooled, reflux condenser. At the expiration of this period, cool the contents of the flask and introduce 50 cubic centimeters of water through the condenser. With the condenser attached, agitate with slight warming until the oily matter in the bottom of the flask has dissolved. Filter when cool, and to the filtrate add a few drops of phenolphthalein. Run in dilute caustic soda (20:1,000) from a burette until just neutral (until the yellow color just changes to reddish yellow). The free acid is thus neutralized. Now run in from a burette a measured quantity, usually about 25 cubic centimeters, of caustic-soda solution of known strength (about twice normal or a little stronger). Heat the contents of flask on a water bath and titrate the excess of caustic soda with normal hydrochloric acid. The percentage of glycerol present, as calculated from the amount of sodium hydroxide used to saponify the triacetin, will be evident from the following calculation:

ILLUSTRATION.—The amount of sodium-hydroxide solution added after neutralization was 27.15 cubic centimeters. Assume that one cubic centimeter of the sodium-hydroxide solution used equals 2.42 cubic centi-

meters of normal hydrochloric acid. Therefore, 27.15 cubic centimeters $\times 2.42 = 65.70$ cubic centimeters, the equivalent of 27.15 cubic centimeters of sodium hydroxide in normal hydrochloric acid.

After saponification, 33.2 cubic centimeters of normal hydrochloric acid was required to neutralize the excess of sodium hydroxide; 65.7 cubic centimeters less 33.2 cubic centimeters equals 32.5 cubic centimeters of normal hydrochloric acid, which is equivalent to the sodium hydroxide required for the saponification of the triacetin. One cubic centimeter of normal acid equals .03069 gram of glycerol, 32.5 cubic centimeters of normal acid equals .99742 gram of glycerol; weight taken for analysis equals 1.2501 grams.

$$\frac{.99742 \times 100}{1.2501} = 79.78 \text{ per cent. glycerol present}$$

97. Bichromate Oxidation Method.—The bichromate oxidation method is based on the fact that 1 gram of glycerol is completely oxidized to carbon dioxide by 7.4564 grams of potassium bichromate in the presence of sulphuric acid. It does not require the skill of manipulation of the acetin method, but unfortunately it does not give as accurate results because of the oxidation of organic matter, other than glycerol, which may also be present. The following reagents are required:

Potassium bichromate.—The very purest salt obtainable is powdered and dried at 140° C. and kept in a tight-fitting glass-stoppered bottle.

Mohr's salt.—$FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$.—Dissolve 3.7282 grams of the dry $K_2Cr_2O_7$ in 30 c. c. of water, add 50 cubic centimeters of 50 per cent. H_2SO_4 and to the cold undiluted solution add a moderate excess of Mohr's salt from a tared weighing bottle. Titrate back the excess of Mohr's salt with the $K_2Cr_2O_7$ solution described later. Calculate the value of the Mohr's salt in terms of $K_2Cr_2O_7$.

Standard $K_2Cr_2O_7$ Solution.—Dissolve 7.4564 grams $K_2Cr_2O_7$ in 1,000 cubic centimeters water. 1 cubic centimeter contains .0074564 gram $K_2Cr_2O_7 = .001$ gram glycerol.

Basic Lead Acetate.—Dissolve 235 grams of lead acetate in 1,000 cubic centimeters of water; boil, and stir in 165 grams of litharge. Boil and stir 15 minutes.

Silver Acetate.—A saturated solution is prepared at ordinary temperatures (about 20° C.).

Dilute Sulphuric Acid.—Add 150 cubic centimeters H_2SO_4 to 850 cubic centimeters of water, with the usual precautions.

The method of procedure is to weigh out 20 grams of the crude glycerine, make up to 250 cubic centimeters, and mix thoroughly. Pipette off 25 cubic centimeters into a 50-cubic-centimeter beaker and add a slight excess of the basic acetate-of-lead solution. Wash several times by decantation, decanting through a filter into a 250-cubic-centimeter graduated flask. Pour precipitate on the filter and wash thoroughly. Add 12 cubic centimeters saturated silver-acetate solution and a slight excess of dilute sulphuric acid (about 5 cubic centimeters) and make it up to the mark with .2 cubic centimeter excess to allow for volume of precipitate. Mix well. Filter through a dry filter and reject first portion, collecting the balance in a glass-stoppered 250-cubic-centimeter flask.

Weigh out 1.8641 grams of the $K_2Cr_2O_7$ into a 150-cubic-centimeter beaker (previously cleaned with $K_2Cr_2O_7$ and H_2SO_4 solution and washed with distilled water). Add 25 cubic centimeters distilled water and then 25 cubic centimeters of the clear filtrate to be tested and stir until the $K_2Cr_2O_7$ is dissolved. Add with constant stirring 25 cubic centimeters of concentrated H_2SO_4, transfer to a steam bath and oxidize for 30 minutes, keeping the beaker covered with an absolutely clean watch glass. Remove from the bath and add a slight excess of Mohr's salt from a tared weighing bottle and titrate back the excess with the standard $K_2Cr_2O_7$ solution, using potassium ferricyanide on a white spot plate as an indicator.

Calculation of Results.—Because of the manner in which the 20-gram sample of crude glycerine was diluted, namely, the 20 grams to 250 cubic centimeters and 25 cubic centimeters of this solution to 250 cubic centimeters, the 25-cubic-centimeter portion of the latter solution, that was treated with potassium bichromate, contains only .2 gram of crude glycerine, or $\frac{1}{100}$ of the original sample. Assume that in this particular analysis, 1.8641 grams of solid $K_2Cr_2O_7$ are added to .2 gram of the crude glycerine, in order to oxidize the glycerol that it contains. This quantity of $K_2Cr_2O_7$ is more than enough to oxidize the glycerol in the .2-gram sample, since

7.4564 grams $K_2Cr_2O_7$ will oxidize 1 gram of glycerol. Therefore $K_2Cr_2O_7$ will be present in excess and the exact excess is determined by means of Mohr's salt and the standard $K_2Cr_2O_7$ solution. Assume that of the particular Mohr's salt used, 8.015 grams were equivalent to 1 gram of $K_2Cr_2O_7$, that 5.4892 grams of Mohr's salt were added to reduce the excess $K_2Cr_2O_7$, and that 7.3 cubic centimeters of the standard $K_2Cr_2O_7$ solution were required to oxidize the excess of Mohr's salt added.

1 c. c. $K_2Cr_2O_7$ solution = .0074564 g. $K_2Cr_2O_7$

7.3 c. c. $K_2Cr_2O_7$ solution = .0544 g. $K_2Cr_2O_7$

1 g. $K_2Cr_2O_7$ = 8.015 g. Mohr's salt

.0544 g. $K_2Cr_2O_7$ = .436 g. Mohr's salt

The excess of Mohr's salt used is then .436 gram. The total quantity of Mohr's salt used was 5.4892 grams. Then,

$$5.4892 - .436 = 5.0532 \text{ grams}$$

of Mohr's salt actually used up in reducing the excess $K_2Cr_2O_7$.

1 g. Mohr's salt = .124 g. $K_2Cr_2O_7$

5.0532 g. Mohr's salt = .6265 g. $K_2Cr_2O_7$, which represents the excess. Then,

$1.8641 - .6265 = 1.2376$ g. $K_2Cr_2O_7$ actually required to oxidize the glycerol in the .2-gram sample.

1 g. $K_2Cr_2O_7$ = .134 g. glycerol

$1.2376 \times .134 = .1658$ g. glycerol in the sample

$$\frac{.1658 \times 100}{.2} = 82.9 \text{ per cent. glycerol in the sample}$$

This is a modification of the general method, but has a great advantage in using the dry salts in place of the concentrated solutions. It gives excellent results.

Glycerol in Filter-Press Cake.—Extract 10 grams of the cake five or six times with boiled, distilled water, using about 350 cubic centimeters in all. Evaporate the filtrate to 75 cubic centimeters; purify with lead acetate, silver acetate, and sulphuric acid by the method just given. The solution is made up to exactly 250 cubic centimeters and one-fifth or one-tenth taken for oxidation. The rest of the analysis is carried out as directed in the method already given.

Glycerol in Recovered Salt.—Extract a 10-gram sample of the salt with an alcohol-ether (1:3) solution. Evaporate the

extract to expel the alcohol and ether. This is done on a steam bath and may be hastened by adding small amounts of water after the extract has been concentrated to a small volume. The alcohol will evaporate quicker if this is done and there is less danger of losing glycerine. When the alcohol has been removed, the extract is diluted, purified, and oxidized by the method given.

SOAP ANALYSIS AND THE INTERPRETATION OF RESULTS

98. Assume that a cake of soap made by the boiled or settled process analyzed as follows:

	Per Cent.
Water	31.27
Fatty anhydride	37.57
Rosin anhydride	20.28
Combined alkali	6.57
Free caustic alkali	none
Free carbonated alkali	2.51
Salt	.21
Unsaponifiable	1.08
Undetermined	.51
	100.00

Then combining the ingredients according to their existing state in the soap, the analysis would appear as follows:

		Per Cent.
Water		31.27
Soap	Combined alkali as Na_2O . 6.57	
	Fatty anhydrides 37.57	. 64.42
	Rosin anhydrides 20.28	
Carbonated alkali, Na_2CO_3		2.51
Salt		.21
Unsaponifiable		1.08
Undetermined (glycerol, etc.)		.51
		100.00

99. It will be assumed that the sample analyzed is a fairly fresh piece of soap, not having undergone much dry-

ing. Settled rosin soap fresh from the cutting table is known to contain from 30 to 35 per cent. of water. The sample is further confirmed as one of a settled soap by the analysis, which shows no free caustic, the absence of much glycerol, and the low percentage of unsaponifiable matter. It is also possible to tell from the appearance of the sample whether the soap is a cold-process or a settled soap. Thus, if it has a broad, open texture resulting from the slow crystallization of

TABLE VIII

ANALYSES OF VARIOUS LAUNDRY SOAPS

Ingredients	1	2	3	4	5	6	7
	Per Cent. of Each Ingredient						
Water	26.30	26.37	29.68	70.14	71.59	28.67	31.18
Fatty anhydride	33.52	30.77	34.23	7.20	8.63	41.69	37.57
Rosin anhydride	24.57	28.89	18.34	none	none	15.06	20.28
Combined alkali	6.54	7.21	6.21	1.33	1.53	6.87	6.57
Free $NaOH$	trace	none	.04	none	.12	none	.02
Free Na_2CO_3	2.14	2.53	2.94	7.87	5.26	2.23	2.01
Sodium silicate	1.24	1.47	2.90	none	none	none	none
Salt	.35	.19	.23	11.28	10.14	.30	.21
Unsaponifiable	3.08		5.36				1.08
Insoluble	2.26	2.49	.07		.23	.48	.08

the sodium stearate in a menstruum of sodium oleate and sodium resinate, it is safe to say that the soap has not been crutched. If the soap is homogeneous in texture, with no marked crystallization, it has been crutched, in which process the texture arising from the slow cooling of the unfilled soap in the frames is broken up by the intimate mixing in the crutcher of the soap formed from fatty acids of different melting points. In Table VIII are given the analyses of various laundry soaps.

CHEMICAL EXAMINATION OF REFINED GLYCERINE

100. Determination of Salt.—To determine the amount of salt in a sample of refined glycerine, 100 cubic centimeters of the sample is diluted with 200 cubic centimeters of water and titrated directly with $\frac{N}{10}$ $AgNO_3$, using potassium chromate as an indicator. For all practical purposes, the weight of 100 cubic centimeters of glycerine is taken as 126 grams.

101. Determination of Ash.—To determine the ash present, weigh out 25 grams of glycerine on the coarse balance into a weighed platinum dish. Heat carefully to ignition and allow combustion to proceed. Expel all carbonaceous matter with a strong Bunsen-burner flame, taking care to lose no salt by volatilization or decrepitation. Cool and weigh on the fine balance. Calculate the percentage of ash as in the preceding case.

102. Higher Fatty Acids.—Pass a stream of nitrogen tetroxide through a portion of the glycerine that is diluted with twice its volume of distilled water and contained in a test tube. After this operation place the test tube on a steam bath and heat for 2 hours. Glycerine that is to be used for the manufacture of nitroglycerine should give no precipitate, either on dilution or later in the operation. Glycerine that will stand this test may be considered free from higher fatty acids.

103. Neutrality.—A glycerine may be considered neutral if, when 50 grams is diluted with twice its weight of distilled water and a few drops of an alcoholic solution of phenolphthalein are added, not more than 1 cubic centimeter of $\frac{N}{4}$ sulphuric-acid or sodium-hydroxide solution is required to produce a change in color.

104. Specific Gravity.—Next to the quality of the glycerine, the specific gravity is the most important test, and

this test requires care and skill for its accurate determination. The instrument used for making the specific-gravity determination is called a *picnometer*. As shown by Fig. 13, it consists of a flask *a* the volume of which is known and which is fitted with a capillary tube *b*. This tube is capped by a glass cap *c*. The joint between the cap and the capillary tube is air-tight because of the fact that the outside of the tube *b* and the inside of *c* have been ground to a perfect fit. This is known as a ground-glass joint. The flask *a* also contains a thermometer *d* which is made to fit tightly by means of the ground-glass joint which it forms with *a* at *e*.

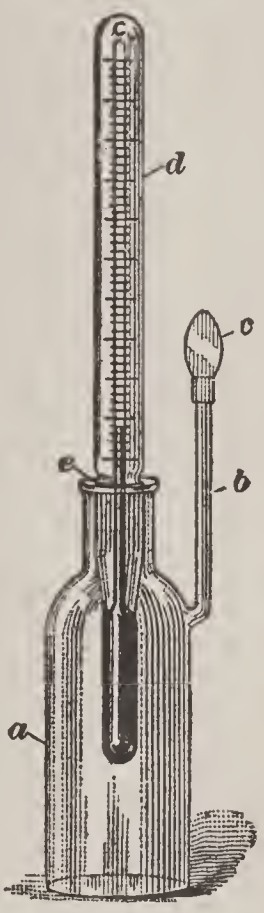

FIG. 13

The sample of glycerine in a glass-stoppered flask is cooled to a temperature of 10 to 12° C. and then transferred to the picnometer, which must be filled. The thermometer is then inserted and seated and the cap *c* removed. The picnometer is placed at once in a bath of ice water up to its neck. The bath is kept at a temperature of 12 to 13° C. by the ice and is well stirred to allow the temperature to rise slowly. The object is to get the temperature of the contents of the picnometer to equal the temperature of the bath at 15.5° C. When this equilibrium is reached, the excess of glycerine is carefully removed from the tip of the capillary tube and the cap put on. The picnometer is then taken from the bath, wiped off until absolutely dry, and allowed to stand in the balance room. When it has reached room temperature it is weighed.

The total weight of the picnometer and glycerine minus the weight of the picnometer, gives the weight of a certain known volume of glycerine. The operation is now carried out with pure water under the same conditions. Then the weight of the glycerine divided by the weight of an equal volume of water at the same temperature gives the specific gravity of the glycerine. Table IX gives the specific gravities of aqueous solutions of glycerine as determined by Gerlach and Skalweit.

TABLE IX—SPECIFIC GRAVITY OF AQUEOUS SOLUTIONS OF CHEMICALLY PURE GLYCERINE

Per Cent. Glycerol	Gerlach		Skalweit	Per Cent. Glycerol	Gerlach		Skalweit
	Sp. Gr. 15° C.	Sp. Gr. 20° C.	Sp. Gr. 15° C.		Sp. Gr. 15° C.	Sp. Gr. 20° C.	Sp. Gr. 15°
0	1.0000	1.0000	1.0000	51			1.1318
1			1.0024	52			1.1346
2			1.0048	53			1.1374
3			1.0072	54			1.1402
4			1.0096	55	1.1430	1.4150	1.1430
5			1.0120	56			1.1458
6			1.0144	57			1.1486
7			1.0168	58			1.1514
8			1.0192	59			1.1542
9			1.0216	60	1.1570	1.1550	1.1570
10	1.0245	1.0235	1.0240	61			1.1599
11			1.0265	62			1.1628
12			1.0290	63			1.1657
13			1.0315	64			1.1686
14			1.0340	65	1.1711	1.1685	1.1715
15			1.0365	66			1.1743
16			1.0390	67			1.1771
17			1.0415	68			1.1799
18			1.0440	69			1.1827
19			1.0465	70	1.1850	1.1820	1.1855
20	1.0490	1.0480	1.0490	71	1.1878	1.1847	1.1882
21			1.0516	72	1.1906	1.1874	1.1909
22			1.0542	73	1.1934	1.1901	1.1936
23			1.0568	74	1.1962	1.1928	1.1963
24			1.0594	75	1.1990	1.1955	1.1990
25	1.0620	1.0610	1.0620	76	1.2018	1.1982	1.2017
26			1.0646	77	1.2046	1.2009	1.2044
27			1.0672	78	1.2074	1.2036	1.2071
28			1.0698	79	1.2102	1.2063	1.2098
29			1.0724	80	1.2130	1.2090	1.2125
30	1.0750	1.0740	1.0750	81	1.2157	1.2117	1.2152
31			1.0777	82	1.2184	1.2144	1.2179
32			1.0804	83	1.2211	1.2171	1.2206
33			1.0831	84	1.2238	1.2198	1.2233
34			1.0858	85	1.2265	1.2225	1.2260
35	1.0885	1.0875	1.0885	86	1.2292	1.2252	1.2287
36			1.0912	87	1.2319	1.2279	1.2314
37			1.0939	88	1.2346	1.2306	1.2341
38			1.0966	89	1.2373	1.2333	1.2368
39			1.0993	90	1.2400	1.2360	1.2395
40	1.1020	1.1010	1.1020	91	1.2425	1.2386	1.2421
41			1.1047	92	1.2451	1.2412	1.2447
42			1.1074	93	1.2476	1.2438	1.2473
43			1.1101	94	1.2501	1.2464	1.2499
44			1.1128	95	1.2526	1.2490	1.2525
45	1.1155	1.1145	1.1155	96	1.2552	1.2516	1.2550
46			1.1182	97	1.2577	1.2542	1.2575
47			1.1209	98	1.2602	1.2568	1.2600
48			1.1236	99	1.2628	1.2594	1.2625
49			1.1263	100	1.2653	1.2620	1.2650
50	1.1294	1.1280	1.1290				

SPECIFICATIONS FOR GLYCERINE

105. The principal specifications for chemically pure glycerine are that it shall be water-white in color, of very slight odor, and have a specific gravity at 25° C. of 1.249; it must be neutral to litmus in a 1:20 water solution; it must not have a total residue on ignition of more than .0105 per cent., of which not more than .007 per cent. of the whole must be mineral matter, and a total chlorine content of more than .001 per cent. calculated as sodium chloride.

106. The following specifications have been prepared by a large consumer for the purchase of dynamite glycerine:

1. Specific gravity. Not less than 1.262 at $\frac{15.5°}{15.0°}$ C.
2. Odor. Slight. No bad odor.
3. Color. Not darker than straw color.
4. Acidity. When 50 cubic centimeters of the glycerine plus 10 cubic centimeters of distilled water free from carbon dioxide are mixed and about $\frac{1}{2}$ cubic centimeter of phenolpthalein indicator (5 g. per liter of 50-per-cent. alcohol) used, it shall not require more than .3 cubic centimeter of normal hydrochloric acid nor more than .3 cubic centimeter of normal sodium-hydroxide solution for neutralization.
5. Ash not over .1 per cent.
6. Chlorine. Not over .01 per cent. chlorine as calculated from a volumetric determination of the chlorine in the aqueous solution of the residue left on ignition.
7. Nitration and separation. When 15 grams are nitrated in a glass vessel with 70 cubic centimeters of a mixture consisting of 37-per-cent. pure nitric acid of 1.5 specific gravity and 63-per-cent. pure sulphuric acid of 1.845 specific gravity, at a temperature not allowed to exceed 20° C., and the whole poured into a glass cylinder of $1\frac{1}{2}$ inches internal diameter, the nitroglycerine should separate so that the line of demarcation will be clear, and there should be practically no so-called flocculent matter present.

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